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Contents

Age from metamict minerals . . . . . J. Laurence Kulp, Herbert L. Volchok, and H. D. Holland 709
South African scheelites and an *x*-ray method for determining members of the scheelite-powellite series . . . . . F. H. S. Vermaas 719
New occurrences of minerals at Iron Mountain, Missouri . . . . . Victor T. Allen and Joseph J. Fahey 736
A test of the accuracy of chemical analysis of silicate rocks . . . . . H. W. Fairbairn and J. F. Schairer 744
Blowpipe petrography . . . . . Wilfrid R. Foster 758
Regularities in the infrared absorption spectra of silicate minerals . . . . . Philip J. Launer 764
Probable identity of belyankite with creedite . . . . . Michael Fleischer 785
New methods for detecting certain crystalline defects in quartz . . . . . Shin-piaw Choong 791
Differential thermal study of Colorado oil shale . . . . . Howard H. Heady 804
Cell size, optical properties and chemical composition of laumontite and leonhardite. With a note on regional occurrences in New Zealand . . . . . D. S. Coombs 812
Development and growth of cordierite in para-lavas . . . . . V. Venkatesh 831
Wardite from Beryl Mountain, New Hampshire . . . Cornelius S. Hurlbut, Jr. 849
A new series of immersion liquids . . . . . Robert Meyrowitz 853
Notes and News: Crystallographic projections nomenclature dilemma . . . . . D. Jerome Fisher 857
  Universal compass and the plunge of the bedded cupriferous pyritic ore deposit in Japan . . . . . Hideki Imai 861
  Lead contamination in Duco cement . . . A. A. Levinson and C. H. Hewitt 864
  Preferred orientation of olivine crystals in troctolite of the Wichita Mountains, Oklahoma . . . . . W. T. Huang and C. A. Merritt 865
Book reviews 871
New mineral names 882

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AGE FROM METAMICT MINERALS*

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ABSTRACT

Various specimens of metamict zircon, samarskite, microlite, fergusonite, pyrochlore, and ellsworthite have been subjected to alpha activity measurement, differential thermal analysis and x-ray diffraction analysis. The ratio of the area under the thermal curve peak, (which is proportional to the lattice disorganization), to the alpha activity increases with the age of the mineral. Furthermore in the case of eleven specimens of samarskite of the same geologic age from the Spruce Pine District it was found that the *DTA* peak area increases with alpha activity over a considerable range. It appears that a new method of age determination is available although much detailed study will be required before accurate geologic dates can be derived.

INTRODUCTION

In an earlier paper, Holland and Kulp (1950), it was suggested on theoretical grounds that metamict minerals might be useful as age indicators. This report presents the experimental results of a preliminary survey of the problem.

The principles involved may be stated rather simply. Internal alpha bombardment of a mineral due to the presence of uranium or thorium series isotopes breaks chemical bonds and disorganizes the lattice. The number of bonds broken depends on the alpha activity, the length of time during which the mineral has undergone bombardment, and the inherent strength of the crystal. The disorganization of the structure may be measured by several methods. Small amounts of lattice disruption can be measured by thermoluminescence techniques (Daniels and Saunders, 1950) and by changes in optical properties. If the concentration of broken bonds is large, measurement of density or of the energy of recrystallization on heating become useful means of determining the amount of lattice disruption. The energy liberated during recrystallization is readily measured by differential thermal analysis. The area under the thermal curve peak related to the recrystallization energy, is proportional to the total lattice disorganization due to the alpha bombardment. Until a saturation value is reached, this should be roughly linear with time for a fixed alpha activity. The alpha activity is determined by direct counting procedures. X-ray diffraction serves to identify the particular phase (mineral) studied. Complete chemical analysis of each specimen would be desirable to assess the effect of substitution on lattice stability but this was not possible in the present reconnaissance study.

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The minerals which have undergone sufficient lattice disruption to be detected by x-ray diffraction or thermal analysis are called metamict. The common representatives are the isodesmic multiple oxides of the type $A_mB_nO_{2mn}$, where $A = \text{U}$, Th, rare earths, Ca, Na, etc., and $B = \text{Nb}$, Ta, Ti, etc. These include pyrochlore-microlite, fergusonite, euxenite-polycrase, eschynite-priorite, samarskite, betafite. Uraninite and thorianite are commonly non-metamict probably due to the simplicity of crystal structure. Zircon is also found in the metamict state.

One of the major problems in this investigation was to procure a sufficient number of samples from enough different localities to demonstrate definite age relations. Another difficulty was presented by the uncertainty in the geologic age of many of the specimens due to the absence or inadequacy of uranium-lead ratio data.

The ultimate "age curve" for a particular mineral structure which can become metamict will be a plot of the ratio of energy of recrystallization to present alpha activity against time.

The authors wish to acknowledge the kind cooperation of Dr. Frederick Pough, Director, American Museum of Natural History and Frank A. Taylor, acting Director U. S. Nat. Museum, who helped us augment the specimens of the Columbia University Mineralogical Collection provided through the kindness of Prof. Paul F. Kerr. The assistance of Mr. Edward Lyden in the laboratory was most helpful.

The measurement of the alpha activity of these specimens was done by the scintillation counting of thin sources. The technique is described in detail elsewhere (Kulp, Holland and Volchok 1951). The differential thermal analysis apparatus and procedure is the same as that previously described (Kulp and Kerr, 1949). The x-ray diffraction patterns were taken at 40 KV, 20 m.a. in a straumanis camera using copper radiation.

RESULTS

A. Zircon

Table 1 summarizes the data obtained on the specimens of zircon which were studied. The "probable geological age" was obtained from

TABLE 1. DATA ON ZIRCON SPECIMENS

GROUP 1. NON METAMICT BY X-RAY DIFFRACTION AND DTA CRITERIA

Locality	Probable Geologic Age in M. Y.	Activity α/mg/min.
Miask, Urals.	350±100	0.1
Ilmen Mts., U.S.S.R.	350±100	0.1
Espailly, France.	300±100	0.40± .05
Ceylon (1).	600±100	1.03± .05
Deer Hill, N.Y.	400±100	1.4 ±0.1
Henderson, N. C.	300±100	2.9 ±0.1
Renfrew Co., Ontario.	1000±200	3.5 ±0.2*
St. Peters Dome, Colo.	800±100	3.7 ±0.2*
Brudinelle, Ont.	600±200	4.0 ±0.2*
Walhalla, S. C.	250± 50	11.2 ±0.4*

GROUP 2. METAMICT

Locality	Probable Geologic Age M.Y.	Activity α/mg/min.	Area/Activity (Arbitrary Units)
Walhalla, S. C.	250± 50	11.2±0.4	0
Norwich, Mass.	250± 50	100 ±5	3
Hybla, Ont. (1)	300±100	662 ±2	1
Hybla, Ont. (2)	300±100	28.4±0.2	6
Madagascar	350± 50	15.2±0.2	6.5
Bedford, N. Y. (1)	375± 50	32 ±2	7
Bedford, N. Y. (2)	375± 50	16.0±0.5	7.5
Minas Geras, Brazil	500±100	52 ±1	13
Ceylon (2)	600±100	15.8±0.1	15
Arendal, Norway	1000±200	50 ±2	3.5

* Slight broadening of high angle lines.

the best U-Pb or U-He age data available. The specimens in Group 1 were not metamict by x-ray or thermal criteria. None of this group give any thermal reaction although several show slight broadening of the high angle x-ray lines, indicative of incipient metamictization. This line broadening appeared only in specimens with alpha activity greater than 3α/mg/min. and an age greater than 200 m.y. Group 2 comprises metamict minerals including border line case (Walhalla) included for comparison. The ratio of area under the thermal peak (which is related to the heat of recrystallization, and thus to the number of bonds broken) to the alpha activity should be related to age for clean zircons of similar composition. It can be seen that the ratio does increase with age. There are only two anomalous specimens, Hybla (1) and Arendal, Norway

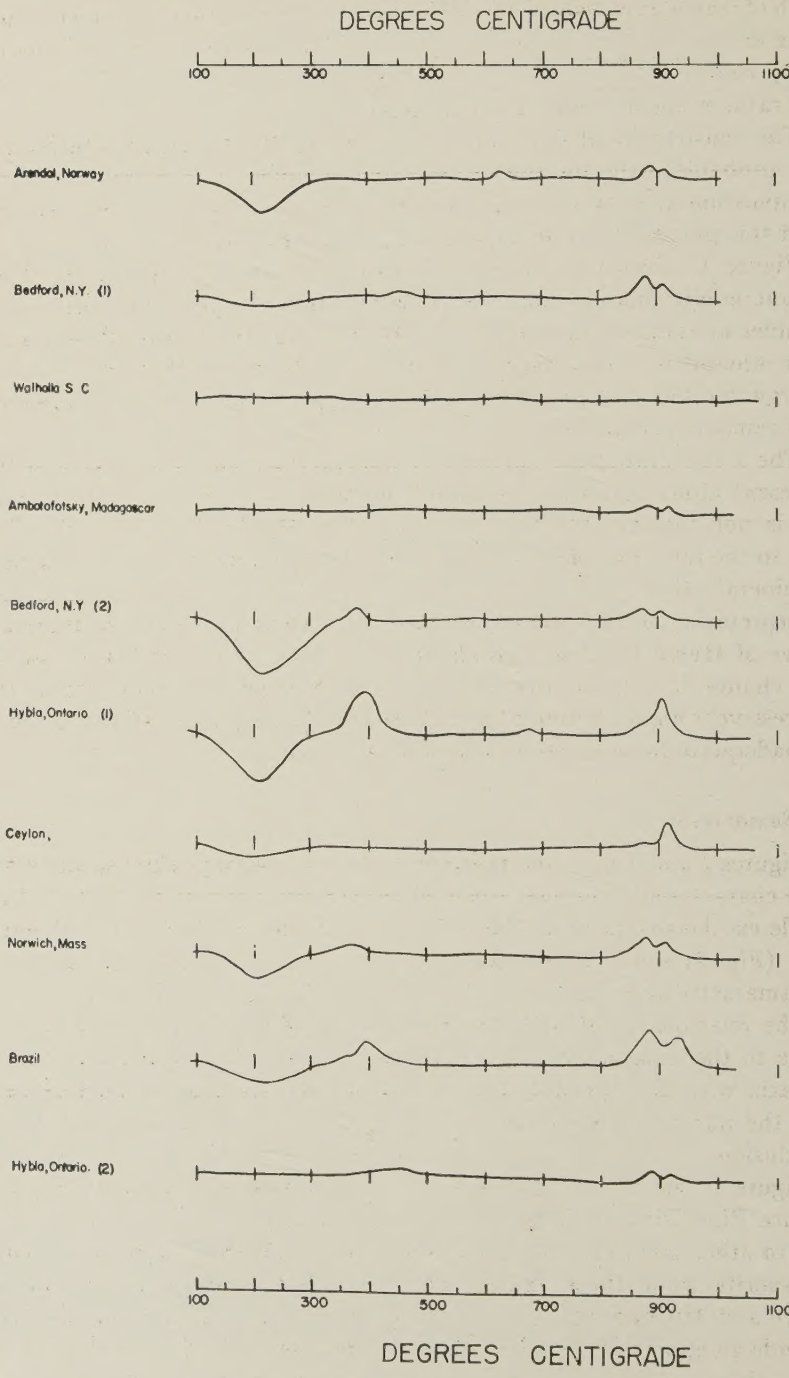
DEGREES CENTIGRADE
100
300
500
700
900
1100
Arendal, Norway
Bedford, N.Y. (1)
Walhalla S C
Ambatofotsky, Madagascar
Bedford, N.Y (2)
Hybla, Ontario (1)
Ceylon,
Norwich, Mass
Brazil
Hybla, Ontario. (2)
100
300
500
700
900
1100
DEGREES CENTIGRADE

FIG. 1

both of which obviously contain at least one other radioactive constituent from an examination of the thermal curve. The foreign constituent apparently contains a large proportion of the alpha active elements so that the ratio is much smaller than expected.

The consistency of the ratios of the two Bedford specimens indicates the probable error for uncontaminated samples of identical chemical composition and the same age with the present technique. It is believed that this precision can be improved by a factor of ten.

Figure 1 shows the thermal curves of the Group 2 specimens. The characteristic thermal curve for metamict zircon appears to consist of a doublet at temperatures of 890 to 910° C. Thus the recrystallization of this mineral is a two-stage process. It will be noted that the relative energy for the two processes varies among the specimens. At present this remains unexplained.

The *x*-ray diffraction patterns of unheated zircons from Hybla with different alpha activities are shown in Plate 1 (*A* and *B*). That Hybla (2) is not considerably less metamict than Hybla (1) is undoubtedly due to the fact that most of the measured alpha activity is derived from a mineral other than zircon in Hybla (1). This is consistent with the interpretation of the area/activity ratio and the extra peak in the thermal curve of Hybla (1) described above. Patterns *C* and *D* of Plate 1 show the change in crystallinity as a result of heating metamict zircons to successively higher temperatures. Note that heating at 1000° for 15 min. is inadequate to completely recrystallize the zircon.

B. Samarskite

Figures 2 and 3 show the thermal curves for the samarskite specimens. The characteristic thermal curve of samarskite appears to consist of a single exothermic peak at 700–710° C. Specimens 2-7, 2-8, 2-9, 2-10 and 2-11 (Fig. 2) show clean *x*-ray (Plate 1 pattern F) diffraction patterns of samarskite after heating, indicative of no foreign constituents.

The relationship of probable geologic age of these samarskite specimens to the area/activity ratio is given in Table 2. A general increase in ratio with age appears, but the Ilmen Mts. specimen is anomalous, and the number of specimens is too small to permit drawing any firm conclusion.

Figure 3 shows thermal curves of samarskite specimens from the Spruce Pine District. Most of these specimens show evidence of peaks due to other minerals. The consistent peak at 450–500° is probably due to priorite while those at 750 may be due to euxenite or eschynite, (Kerr and Holland 1951). The eleven specimens from the one district provide an opportunity to test the metamict age method in another way. Since these are all of the same age, although varying considerably in

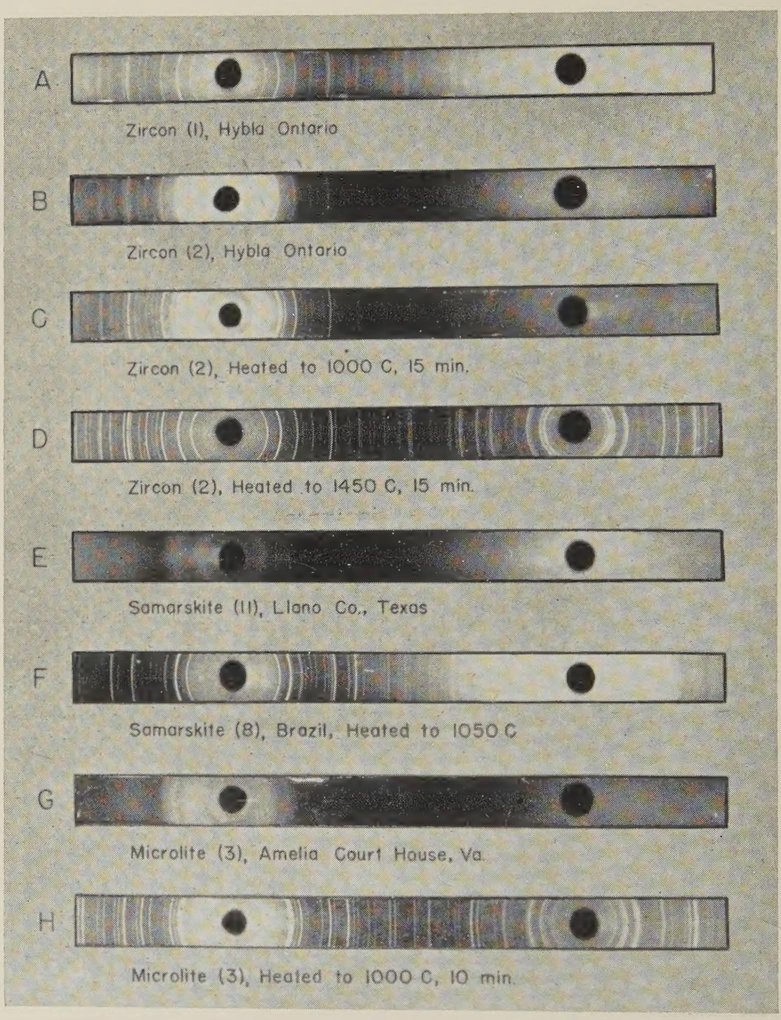
A
Zircon (1), Hybla Ontario
B
Zircon (2), Hybla Ontario
C
Zircon (2), Heated to 1000 C, 15 min.
D
Zircon (2), Heated to 1450 C, 15 min.
E
Samarskite (11), Llano Co., Texas
F
Samarskite (8), Brazil, Heated to 1050 C
G
Microlite (3), Amelia Court House, Va.
H
Microlite (3), Heated to 1000 C, 10 min.

PLATE 1

TABLE 2: AGE RELATIONSHIPS OF SAMARSKITE SPECIMENS

Locality	Probable Geologic Age	$\frac{\text{DTA area in cm.}^2}{\alpha\text{/mg./min.}} \times 1000$
Spruce Pine, N. C.	250 ± 50	15
Canyon City, Colo.	350 ± 100	18
Minas Gerais, Brazil	500 ± 100	21
Llano, Texas	1000 ± 200	33
Ilmen Mts., U.S.S.R.	350 ± 100	35

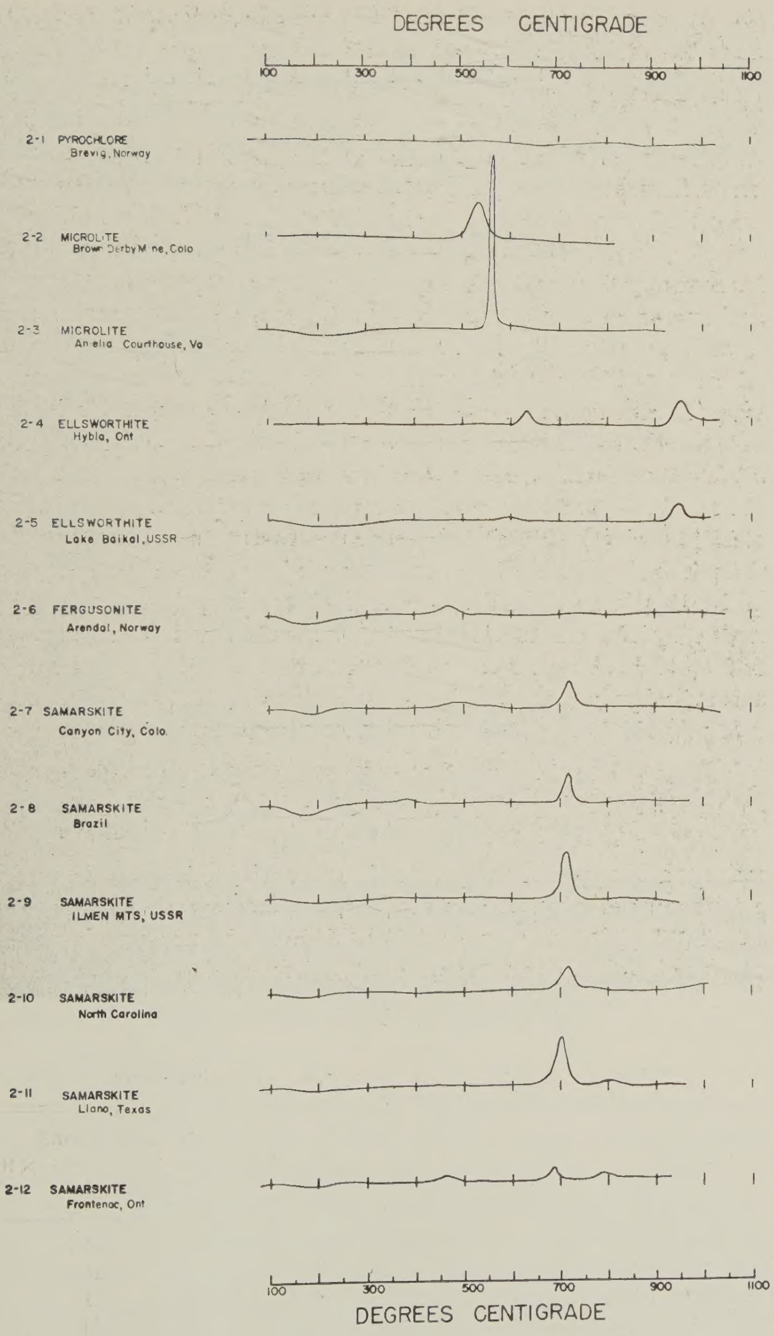
DEGREES CENTIGRADE
100
300
500
700
900
1100
2-1 PYROCHLORE
Brevig, Norway
2-2 MICROLITE
Brown Derby Mine, Colo
2-3 MICROLITE
Amelia Courthouse, Va
2-4 ELLSWORTHITE
Hybla, Ont
2-5 ELLSWORTHITE
Lake Baikal, USSR
2-6 FERGUSONITE
Arendal, Norway
2-7 SAMARSKITE
Canyon City, Colo.
2-8 SAMARSKITE
Brazil
2-9 SAMARSKITE
ILMEN MTS, USSR
2-10 SAMARSKITE
North Carolina
2-11 SAMARSKITE
Llano, Texas
2-12 SAMARSKITE
Frontenac, Ont
100
300
500
700
900
1100
DEGREES CENTIGRADE

FIG. 2

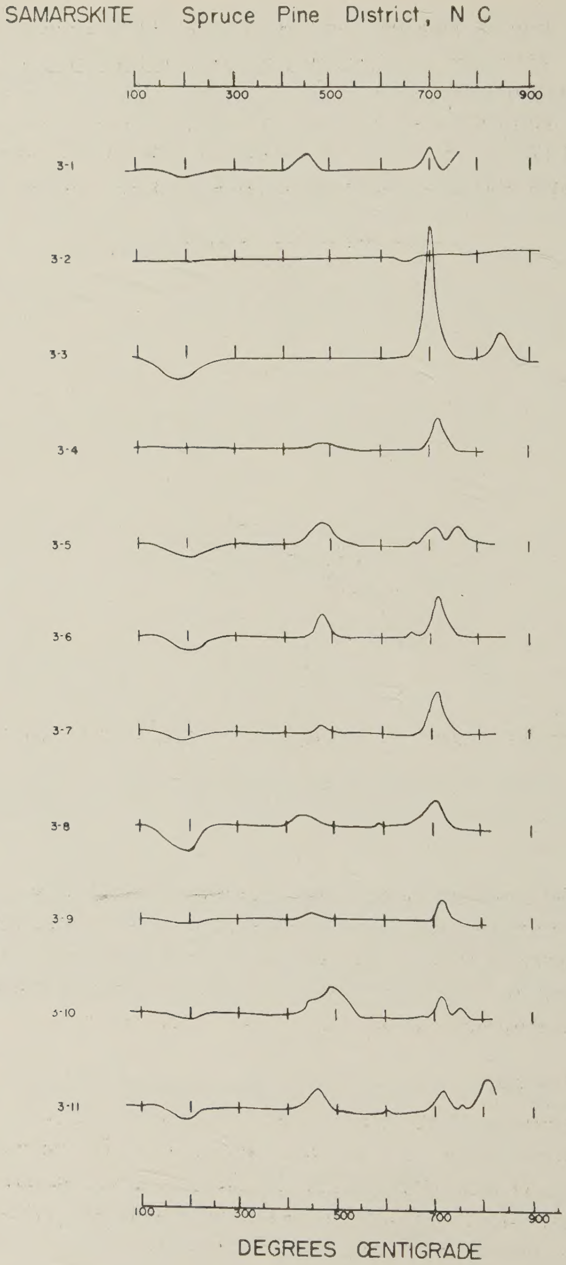
SAMARSKITE Spruce Pine District, N C
100
300
500
700
900
3-1
3-2
3-3
3-4
3-5
3-6
3-7
3-8
3-9
3-10
3-11
100
300
500
700
900
DEGREES CENTIGRADE

FIG. 3

activity, the plot of thermal peak area to activity should be a simple relationship. Figure 4 is a plot of this data over a four fold range in activity. Two important observations can be made. (1) There is a simple linear relationship between area and activity for specimens of the same locality, and (2) for this level of activity in the mineral samarskite, at an age of about 300 m.y., the rate of lattice destruction has not started to level off. If such saturation were reached it would only be possible to estimate a minimum age. That the data for these specimens follow the curve as closely as they do suggests that most of the activity is present in the samarskite. A corollary would be that priorite and exuenite yield greater lattice disruption per alpha than samarskite.

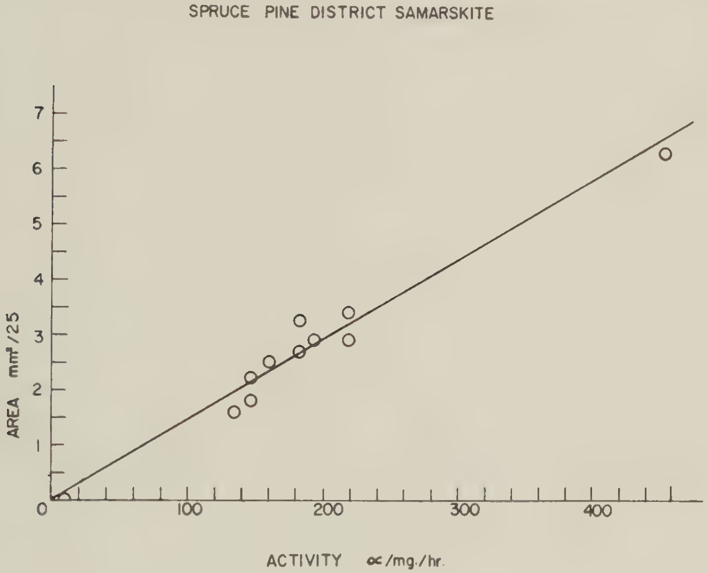

Fig. 4

C. Other Minerals

A few specimens of other minerals which have been reported to occur in the metamict state were studied. Figure 2 shows thermal curves for pyrochlore, microlite, ellsworthite (?) and an impure samarskite (2-12). Only the pyrochlore and microlite were identified with certainty by the x-ray diffraction method. Note from Plate 1, G & H that metamict microlite from Amelia Courthouse, of similar age and greater activity than the samarskite from North Carolina, still retains most intense diffraction lines of crystalline microlite. This suggests that the structure of minerals in the pyrochlore-microlite series is more stable than that of samarskite. That the pyrochlore specimen gave no observable thermal peak is not surprising in view of its lower activity.

The difference in the sharpness of the peaks in the microlite specimens from Brown Derby and Amelia Courthouse is probably related to crystallite size which in turn is affected by the rate of formation of the mineral and the type and extent of substitution. Many of the multiple oxide minerals containing radioactive constituents show very sharp exothermic peaks indicative of a narrow range in crystallite size (Kerr & Holland, 1951); however samarskite appears to be an exception to this. The shape of the peaks is also affected by the rate of heating but these curves are comparable because a constant heating rate was employed.

Ellsworthite appears to be characterized by a single exothermic peak at about 950° C.

Conclusions

(1) A preliminary study of the relationship of alpha activity, degree of lattice destruction and age of metamict minerals suggests that if the first two of these factors may be measured, the age may be estimated.

(2) *DTA* can be used to measure the amount of lattice disorganization if the number of chemical bonds broken per gram is sufficiently great.

(3) For a set of specimens of a given age, the lattice disruption increases directly as the alpha activity providing the age is not too great.

(4) If more detailed work is carried out in which all of the mineral phases present in each sample, the crystallite size, and the nature of the substitution in each phase are quantitatively determined, it should be quite possible to arrive at reasonably accurate ages for rocks containing metamict minerals. To do this it must be possible to obtain unweathered samples. Also it must be assumed that temperature effects since the early history of the rock have been negligible.

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SOUTH AFRICAN SCHEELITES AND AN X-RAY METHOD FOR DETERMINING MEMBERS OF THE SCHEELITE-POWELLITE SERIES

F. H. S. Vermaas, *Geological Survey, Pretoria, South Africa.*[*]

Abstract

A detailed description of the physical and chemical properties of ten South African scheelites and of the synthetic $CaWO_4$-$CaMoO_4$ series is given. Three variation diagrams of values of 2θ with chemical composition of this series are also given, by means of which the MoO_3 content of a member can accurately be determined from its *x*-ray diffraction angles to within 1%.

Introduction

Powellite ($CaMoO_4$), although less common than scheelite ($CaWO_4$), is found at several localities in North America and also at Minusinsk, Siberia. Scheelite free from molybdenum is very rare in nature, the replacement of W by Mo being usually of the order from 1 to 15 per cent. The same range appears to apply to the replacement of Mo by W in natural powellites. These indications that scheelite and powellite may form an isomorphous series is strongly supported by the fact that the ionic radii of hexavalent W and Mo are both 0.68 Å (11, p. 167).

Scheelites from ten localities in South Africa were examined but not one contained more than 2 per cent MoO_3. Neither natural powellite nor other intermediate members of the postulated scheelite-powellite series were available. However, the end-members as well as some intermediate members were successfully synthesized.

The *x*-ray diffraction patterns, and hence also the crystal structures of synthetic $CaWO_4$ and $CaMoO_4$ are identical with those of natural scheelite and powellite, respectively. At the same time an *x*-ray method was devised for determining the composition of a member of the series in terms of its end-members to an accuracy of 2 per cent $CaMoO_4$, or about 1.5 per cent MoO_3 by weight.

The natural scheelites examined in this research came from the following South African localities:

Specimen Number	*Locality*
1	Gwelo dist., Southern Rhodesia.
2	Schurry's Claim, Natos Mine, South West Africa.
3	Joffe's Claim, Groendoorn River, Cape Province.
4	Boksputs, Gordonia, Cape Province.
5	Jackalswater, Namaqualand, Cape Province.
6	Leydsdorp, Transvaal.

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Specimen Number	*Locality*
7	"Altemooi," Steinknopf, Namaqualand, Cape Prov.
8	Stavoren Mine, Potgietersrust, Transvaal.
9	Forbes Reef, Swaziland.
10	Glynn's Reef, Vaalhoek, Pilgrimsrust, Transv.

CHEMICAL PROPERTIES

Samples from the localities listed above were analyzed chemically and spectrographically. Material used for these analyses was examined microscopically and no impurities or inclusions could be seen.

SPECTROGRAPHIC ANALYSES

No attempt was made to compare the intensities of the Ca-or W-lines as these constituents and Mo were determined chemically. When the intensities of the Mo-line (3,903 Å) for different scheelites were compared visually, variations in the intensity of this line were in very good agreement with the relative amounts of MoO_3 determined chemically.

The results obtained on other minor constituents and listed in Table 1, represent a rough semi-quantitative guide of the abundance of these minor constituents. It is considered that none of these is present in quantities exceeding 0.5 per cent. The intensity of each element-line has been visually estimated using an arbitrary scale from zero to 10. This allows a comparison vertically, but not horizontally, in Table 1.

TABLE 1. SPECTROGRAPHIC ANALYSES OF 10 SCHEELITES, SOUTH AFRICA

Sample No.	Si 2,882	Al 3,962	Mg 2,852	Sr 4,607	Ba 4,554	K 4,044	Na 3,302	V 3,184	Fe 3,581	Mn 4,031	Cr 4,275	Ti 3,235	Cu 3,274
1	10	10	8	tr.	0	3	0	8	0	0	2	4	2
2	8	10	6	2	10	0	0	4	0	0	0	0	10
3	10	8	0	tr.	0	0	0	9	2	10	0	0	4
4	7	1	0	1	0	2	0	6	0	0	0	10	1
5	0	5	4	4	2	0	10	10	1	0	0	2	0
6	10	9	7	10	3	10	6	3	0	2	6	8	4
7	4	6	0	2	4	0	1	0	0	1	0	0	0
8	6	4	tr.	1	0	6	0	10	8	10	10	0	0
9	2	1	10	0	1	0	0	6	6	8	8	2	0
10	7	10	0	0	0	1	0	10	10	3	0	1	0

Samples were arced in hollowed copper anodes, (the cathodes were slightly pointed) for 20 seconds at 5 amps (for Cu. analyses carbon electrodes were used). A large Hilger Littrow-type spectrograph was available.

The following elements were absent in all scheelites: Ta, Nb, Pb, As, Bi, Y, Yb, Ce, In, Sb, Li, Zr, B, Rb, Cs, Be.

TABLE 2. CHEMICAL ANALYSES OF 10 SCHEELITES, SOUTH AFRICA

Sample No.	Percentages by Weight of Components*							
	CaO	WO_3	MoO_3	SrO	CuO	Total	% $CaWO_4$	% $CaMoO_4$
1	18.96	77.00	<.0004	—	—	95.96	96.0	0
2	18.87	76.40	0.96	—	0.54	96.77	94.84	1.33
3	19.20	78.30	0.54	—	—	98.04	97.17	0.75
4	18.70	77.63	0.039	—	—	96.37	96.25	0.05
5	19.20	78.36	0.070	—	—	97.63	97.50	0.10
6	18.80	75.16	0.0062	0.46	—	94.43	93.30	0.09
7	19.68	77.08	1.87	—	—	98.63	95.67	2.62
8	19.60	78.84	0.0004	—	—	98.44	97.86	0
9	19.44	78.64	0.0023	—	—	98.08	97.61	0
10	19.36	78.68	<.0004	—	—	98.04	97.66	0

* Chemical analyses by C. J. Liebenberg, Division of Chemical Services, Pretoria.

From Table 2 it appears that all the specimens contain impurities. However, these were not visible under the microscope or ultra-violet lamp.

In the calculation of the norm, an excess of CaO was often found after all the WO_3 and MoO_3 had been allocated to CaO to form the scheelite and powellite molecules. This excess of CaO may be linked with the silica, alumina, or vanadium, the most common elements present in the scheelites. In sample No. 2 a small quantity of Ca was replaced by Cu, and in No. 6 Sr replaced some Ca. These minor replacements of Ca by Cu and Sr caused some deviations in many values of 2θ for many of the reflections in their *x*-ray diffraction patterns.

SYNTHESIS OF MEMBERS OF THE SCHEELITE-POWELLITE SERIES

Pure $CaWO_4$ and $CaMoO_4$ were synthesized by the Manross method (13) by fusing $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$, respectively, with

$CaCl_2 \cdot 2H_2O$. The melting points of these substances, when they have lost their water of crystallization, are as follows:

$CaCl_2 = 772°$ C.
$Na_2WO_4 = 698°$ C.
$Na_2MoO_4 = 687°$ C. (1, p. 369)

Intermediate members containing 20%, 40%, 60% and 80% $CaMoO_4$ were synthesized as follows: pure $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were mixed in the required proportions to yield the aforementioned members of the series. These mixtures were then melted in an open crucible over a bunsen flame and thoroughly agitated to ensure a high degree of homogeneity before adding $CaCl_2 \cdot 2H_2O$. The mixture is then heated for another 15 minutes before cooling.

By grinding the product to about 200 mesh and boiling with water, all of the NaCl formed in the reaction as well as all excess reagents were removed. The final products were dried at 150° C.

The chemicals employed in the syntheses were analyzed reagents which contained alkalies as major impurities but in quantities not exceeding 0.2%. Other impurities were SO_4^{2-}, Pb, Fe, Ba and NH_4OH, but none was present in quantities greater than 0.005%. Spectrographic analyses proved that no Mn, V, Cr, Cu, Si, Sr, Ti, Be, Mg, or Al were present in the reagents, and tended to confirm the manufacturer's analyses.

FLUORESCENCE

Natural scheelites as well as all synthetic mixtures fluoresced when exposed to ultra-violet light ($\lambda = 2536$ Å), the synthetic material showing a somewhat brighter fluorescence than the corresponding minerals. The fluorescent colors of the minerals and their MoO_3 content are listed in Table 3.

TABLE 3. FLUORESCENCE COLORS, 10 SCHEELITES, SOUTH AFRICA

Specimen No.	% MoO_3 (Wgt.)	Fluorescent Color
1	<.0004	Pale blue
2	0.96	Yellow
3	0.54	White
4	0.039	Pale blue
5	0.070	Pale blue
6	0.0062	Pale blue
7	1.87	Yellow
8	0.0004	Pale blue
9	0.0023	Pale blue
10	<.0004	Pale blue

The fluorescence of the synthetic $CaWO_4$ was pale blue, similar to that of the seven samples poor in MoO_3 (Table 3), but all the other synthetic samples showed a yellow fluorescence. A sample containing about 0.5% MoO_3 was also synthesized, and it fluoresced white like the natural mineral of about the same composition (No 3).

R. S. Cannon, K. J. Murata and F. S. Grimaldi of the United States Geological Survey worked out the variation of fluorescence of scheelite with molybdenum content quantitatively with great success (14, p. 65). The variation in fluorescent color that they observed in the natural scheelites was confirmed by preparing synthetic samples of identical chemical composition, and the resulting method they suggested comprises the comparison of the fluorescent color of a scheelite of unknown molybdenum content with the fluorescent colors of a standard series containing scheelites with 0.05, 0.19, 0.33, 0.48, 0.72, 0.96, 1.4, 2.4, 3.4, and 4.8 per cent molybdenum. By employing this method the molybdenum content of scheelites containing less than 4.8 per cent of molybdenum can easily be determined to an accuracy exceeding any industrial requirements.

This pioneering work is of great importance in the industry, the only difficulty is that the molybdenum content cannot, according to this method, be determined accurately in samples containing more than about 5 per cent of molybdenum.

In a detailed study Greenwood (2, pp. 56–64) also noticed a change in fluorescence of scheelite from blue to yellow with increasing molybdenum content, but also related the fluorescence to some impurities, especially manganese. In view of his findings, and the presence of Mn, Fe, and especially V in some of the South African scheelites, some experiments were made by incorporating these components in some synthetic material. First, scheelites were prepared by adding quantities of Mn, Fe, and V varying from about 0.01% to 1% to $Na_2WO_4 \cdot 2H_2O$ and $CaCl_2 \cdot 2H_2O$. (These impurities were added in the form of FeO, $FeCl_2$, MnO, $MnCl_2$, and V_2O_5). However, the fluorescent pale blue color remained unchanged. The procedure was then repeated in the preparation of pure powellite; the fluorescent bright yellow color remained constant.

For MoO_3 percentages greater than about 1% the fluorescent color remains yellow but becomes somewhat brighter with increasing molybdenum content. Hence the intensity may serve as a rough guide to the content of MoO_3 in the scheelite-powellite series in this range of composition. However, this method must be considered unreliable not only because of difficulties in the direct measurement of intensities but also because other factors as yet unknown may influence the intensities. Marden and Meister (16) have studied the decrease in fluorescence intensity caused by various foreign elements when incorporated in synthetic scheelite.

SPECIFIC GRAVITY DETERMINATIONS

Two ordinary quartz specific gravity bottles of about 7 cc. capacity were employed. Triple distilled water which was freed from air was used. All possible precautions were taken to reduce evaporation to a minimum. Air bubbles adhering to the particles were completely removed by heating the bottle with the particles and about $\frac{3}{4}$ of its volume of water to about 60° C. under diminished pressure. Corrections were also made for the difference in the displacement of air by the volume of the contents of the pyknometers and the volume of the weights used with the balance.

Three determinations were made on different portions of each sample and the differences did not exceed 0.005. The results given below may therefore be considered correct to the nearest unit in the second decimal place.

TABLE 4. SPECIFIC GRAVITY, 10 SCHEELITES, SOUTH AFRICA

Sample No.	Specific Gravity (G_4^{25})	% MoO_3 (wgt.)
1	6.08	<0.0004
2	6.01	0.96
3	6.02	0.54
4	6.10	0.039
5	6.08	0.070
6	5.72	0.0062
7	6.00	1.87
8	6.09	0.0004
9	6.12	0.0023
10	6.06	<0.0004

The specific gravities of scheelites containing less than 0.5% MoO_3 are fairly constant, but that of sample No. 6, which contains 0.46% SrO is substantially different from the others. This reduction in specific gravity may be due to the expansion of the unit cell owing to the replacement of Ca with ionic radius of 1.06 Å by Sr with radius 1.27 Å (11, p. 168). On the other hand, this replacement should tend to increase the specific gravity because the atomic weight of Sr is more than twice that of Ca.

The following parameters are given in the literature:

Bragg (4, p. 133)		*Sillen and Nylander (5, pp. 1–27)*
$CaWO_4$: $a=5.24$ Å, $c=11.28$ Å	:	$CaWO_4$: $a=5.23$ Å, $c=11.348$ Å
$CaMoO_4$: $a=5.23$ Å, $c=11.44$ Å	:	$CaMoO_4$: $a=5.21$ Å, $c=11.426$ Å

If the specific gravities of scheelite and powellite are calculated from:

$$d = nM/Nv \cdots (1) \quad (3, \text{p. } 108)$$

where

$n = 8$ for the scheelite group.
$M =$ molecular weight.
$N =$ Avogadro's Number $(6.0597 \pm .0016) \times 10^{23}$ Å
$v =$ Volume of the unit cell.

the following values are found.

Bragg		*Sillen and Nylander*
$CaWO_4$: Sp. Gr. = 6.141	:	$CaWO_4$: Sp. Gr. = 6.125
$CaMoO_4$: Sp. Gr. = 4.231	:	$CaMoO_4$: Sp. Gr. = 4.253

Since the volumes of the unit cells of powellite and scheelite are practically the same, the variation of the density in this series will be a function of the molecular weight, or a function of the MoO_3 content.

Using the unit cell dimensions of two intermediate members of the powellite-scheelite series given by Ödman (7), their specific gravities were calculated according to formula (1). The results are:

(a) Sample with 22.1% MoO_3.	Sp. Gr. 5.56
(b) Sample with 59.3% MoO_3.	Sp. Gr. 4.60

The available specific gravity data suggest the simple relationship presented in Fig. 1.

The specific gravities of the South African scheelites are below 6.13 (calculated sp. gr. for pure $CaWO_4$), and thus may be due to the fact that all the natural scheelites contain impurities in the form of silica, alumina, and vanadium, causing the experimental values to be lower than the calculated ones.

Refractive Indices

The refractive indices of natural and synthetic scheelites were determined according to a single variation method using phosphorus liquids as described by West (6, pp. 245–249). Grains were orientated on a Universal Stage and the indices matched at room temperature by adjusting the wavelength of a monochromator. All indices are given for Na-light at 22° C. and are correct to ±.003. The variation in refractive index from powellite to scheelite offers a fair method of determining the MoO_3 content of a member of this series. The refractive indices of the South African scheelites, except for samples Nos. 2 and 6 varied as follows.

ω from 1.914 to 1.926 and
ϵ from 1.931 to 1.939

The average of the refractive indices of the scheelites containing less than 0.5% MoO_3 are as follows:

$$\omega = 1.921\ (\pm .003)$$
$$\epsilon = 1.938\ (\pm .003)$$

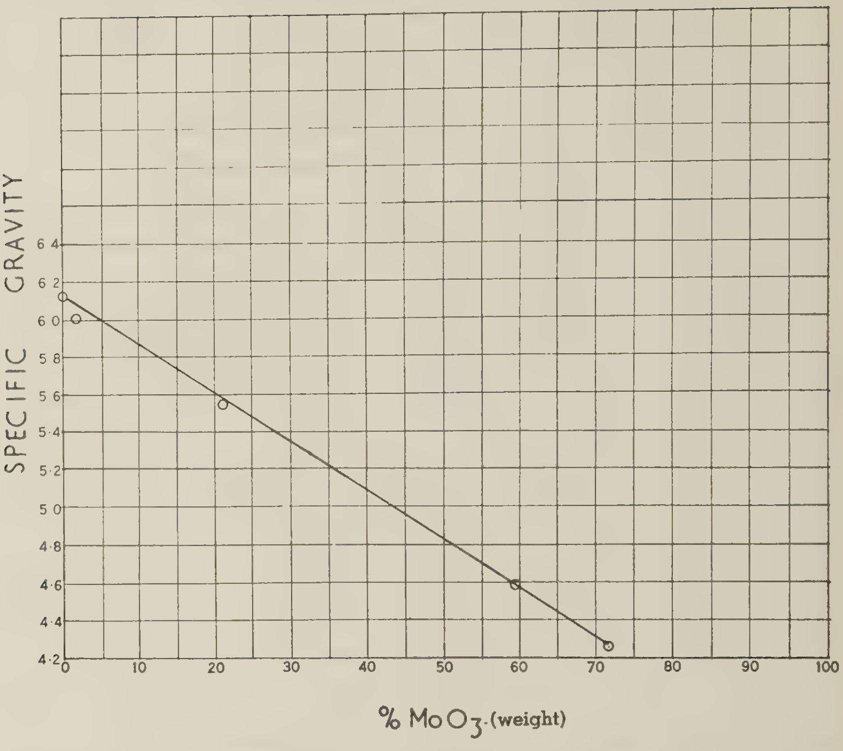

FIG. 1. Graphical representation of the variation of the specific gravity of members of the $CaWO_4$-$CaMoO_4$ series. No specific gravity determinations was attempted on the synthesized members because of their very fine grain size.

The following refractive indices were found for the synthetic material:

	100% $CaWO_4$	20% $CaMoO_4$	40% $CaMoO_4$	60% $CaMoO_4$	80% $CaMoO_4$	100% $CaMoO_4$
ϵ	1.935	1.946	1.954	1.967	1.973	1.984
ω	1.920	1.932	1.942	1.951	1.966	1.974

The refractive indices for natural and artificial scheelite are identical within the limits of errors viz. $\omega = 1.921$ and 1.920, respectively.

The birefringence (ϵ-ω) for the synthetic series decreases from 0.015 for $CaWO_4$ to 0.010 for $CaMoO_4$.

The refractive indices of sample No. 6 which contained 0.46% SrO was found to be:

$$\omega = 1.912\ (\pm .003)$$
$$\epsilon = 1.925\ (\pm .003)$$

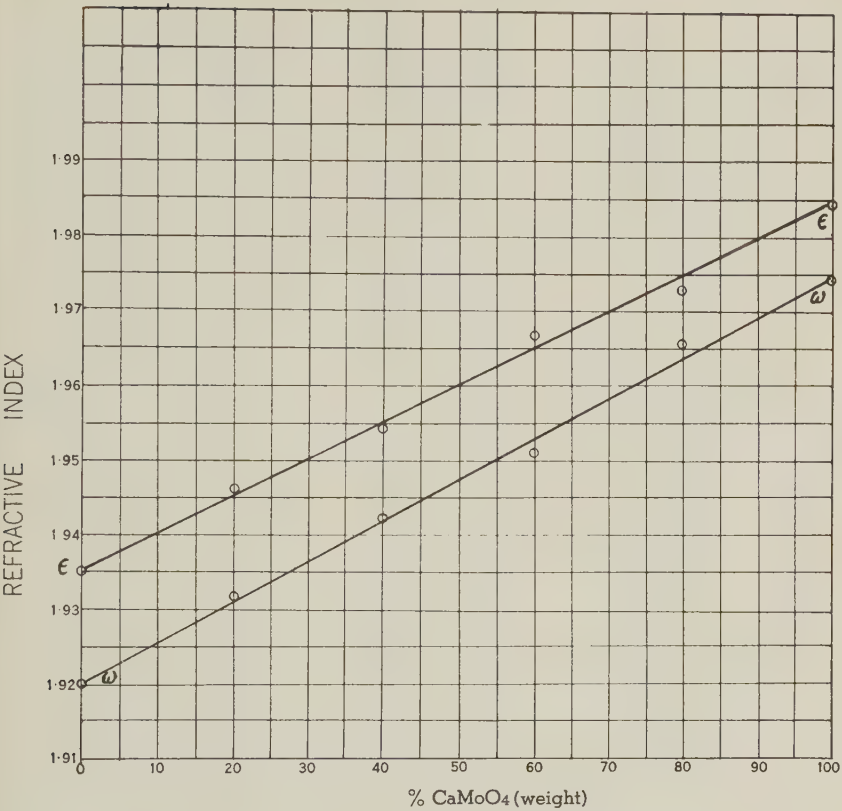

FIG. 2. Graphical representation of the variations of the refractive indices ω and ϵ with the chemical composition of the synthetic $CaWO_4$-$CaMoO_4$ series.

For sample No. 2 which contained 0.54% CuO the refractive indices are:

$$\omega = 1.930\ (\pm .003)$$
$$\epsilon = 1.947\ (\pm .003)$$

The specific refractive energies of WO_3 and MoO_3 were calculated according to Larsen and Berman (15, pp. 30–31) as 0.133 for WO_3 and 0.233 for MoO_3. It will be noticed that Larsen and Berman (15, p. 31) quoted exactly the same specific refractive energy for WO_3 but the calculated value for MoO_3 differs greatly from the 0.241 as given by them.

X-RAY EXAMINATION

X-ray powder diffraction patterns were obtained by using 114 mm. diameter cameras in which the film is mounted according to the Straumanis method (9, p. 726). The time of exposure was 2½ hours using unfiltered Cu-radiation at 35 K.V. and 20 m.a. The temperature during the exposures did not vary more than 1° C. above room temperature (22° C). The variations in room temperature for different exposures did not exceed 3° C.

The films were allowed to dry for two weeks before measuring. The centers of the entrance and exit holes in the film were determined by the accurate measurement of the lines on either side of these holes in order to obtain "check points" from which a shrinkage correction factor was determined.

Table 5. *X*-ray Data on 10 Scheelites, South Africa

No.	Int. (est)	Average of samples 1, 3, 4, 5, 8, 9 and 10		Sample No. 2 containing 0.54% CuO		Sample No. 6 containing 0.46% SrO	
		2θ (Cu)	*d* Å	2θ (Cu)	*d* Å	2θ (Cu)	*d* Å
1	10	29.01	3.08	29.05	3.07	28.99	3.08
2	8	47.30	1.923	47.41	1.918	47.30	1.923
3	9	58.05	1.589	58.19	1.585	58.08	1.588
4	8	59.71	1.549	59.75	1.547	59.58	1.552
5	9	76.41	1.247	76.42	1.246	76.30	1.248
6	8	90.76	1.082	90.70	1.083	90.70	1.082
7	7	99.43	1.010	99.41	1.010	99.27	1.011
8	8	117.02	0.9033	116.90	0.9039	117.02	0.9033
9	8	142.99	0.8122	142.97	0.8123	142.85	0.8127
10	9	150.91	0.7958	150.92	0.7957	150.74	0.7961
11	8	152.13	0.7936	152.01	0.7938	151.87	0.7941
12	8	165.53	0.7764	165.80	0.7762	165.50	0.7765

All reflections with $2\theta > 90°$ are α_1 reflections.

The measuring of the films was carried out as described by Wasserstein (8, p. 106). The films were measured four times using different parts of the scale in order to eliminate any possible errors due to incorrect calibration of the measuring scale or vernier. Each line was measured 5 times at the four different positions in which the film was placed on the scale. The more prominent lines were measured 10 times. The variations in 2θ did not exceed 0.05 degrees for different positions along the scale and all values given in Tables 6 and 7 are hence considered correct to 0.03 degrees.

The variations in 2θ of corresponding lines for those scheelites containing less than 1% MoO_3 never exceeded 0.06 degrees, but larger devia-

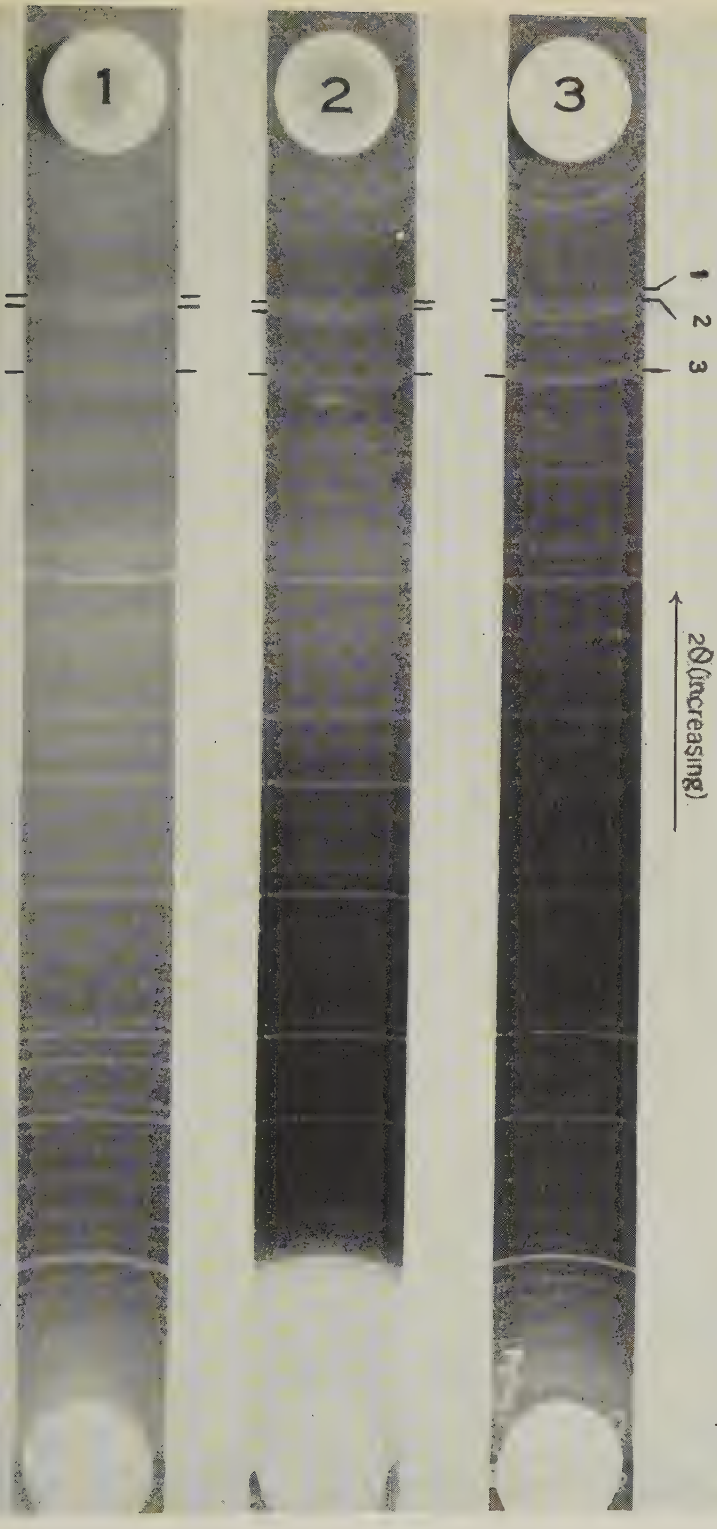

FIG. 3. X-Ray powder patterns of: 1. Natural scheelite, 2. Synthetic $CaWO_4$, 3. Synthetic $CaMoO_4$.

tions from these values of 2θ for corresponding lines were found in samples Nos. 2 and 6, which contained CuO and SrO, respectively. *X*-ray diffraction angles were converted into interplanar spacings by using suitable tables (10).

The above mentioned deviations of 2θ for the more prominent reflections for samples Nos. 2 and 6 form the 2θ values for scheelites containing little MoO_3 are listed in Table 5.

Table 5 illustrates that the partial replacement of Ca by Cu and Sr causes definite line shifts, but these are irregular. Although both samples contain some MoO_3 it is clear that this deviation in 2θ is not due to the MoO_3 content. The replacement of W by Mo causes a systematic shifting of lines as will be pointed out below. A detailed study of the Sr and Cu-bearing scheelites seems desirable.

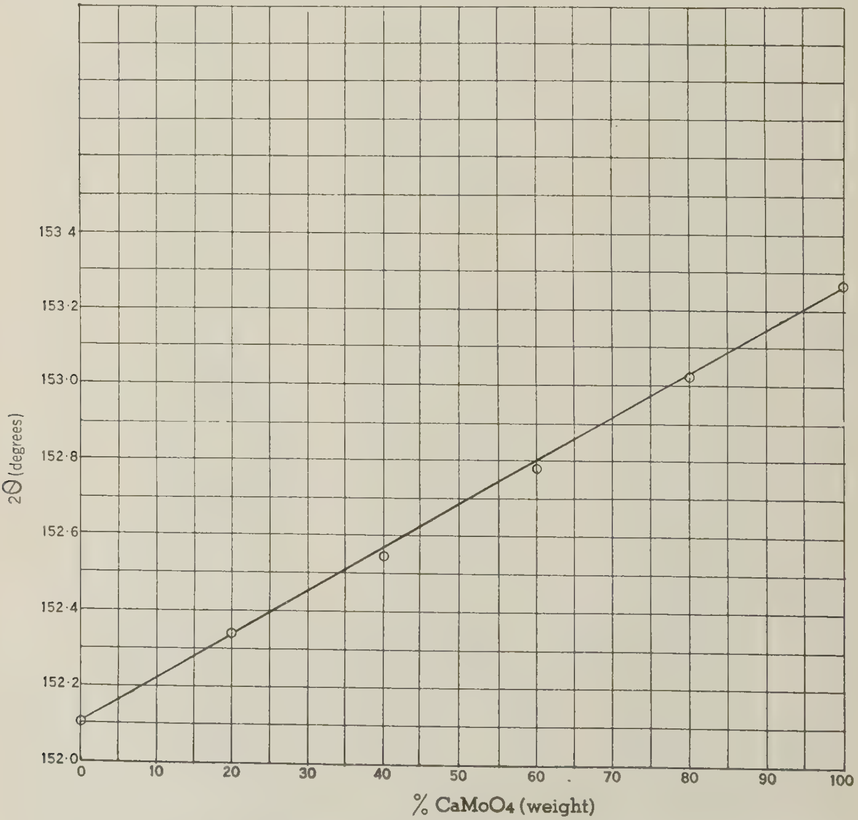

FIG. 4. Variation of 2θ for line No. 1 with variation in the chemical composition of the scheelite-powellite series.

AN *X*-RAY METHOD FOR DETERMINING THE CHEMICAL COMPOSITION OF MEMBERS OF THE SCHEELITE-POWELLITE SERIES

Members of this series may be considered to form solid solutions with complete solubility between the end-members $CaWO_4$ and $CaMoO_4$.

With the usual limitations the composition of any member of the series can be determined fairly accurately from its specific gravity or its refractive indices (Figs. 1 and 2, respectively). More accurate determinations can be made by means of *x*-ray diffraction analyses, with advantages inherent in this method. For this purpose diagrams have been prepared (see Figs. 4, 5 and 6) based on synthetic material and verified with available natural scheelite containing up to 2.62 per cent of $CaMoO_4$

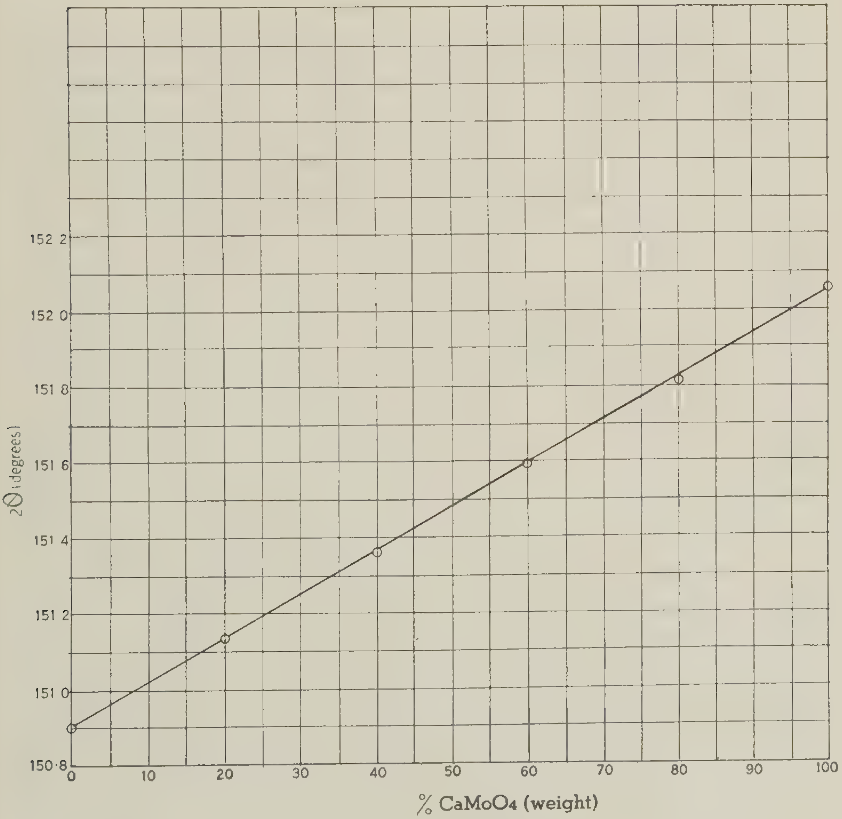

FIG. 5. Variation of 2*θ* for line No. 2 with variation in the chemical composition of the scheelite-powellite series.

TABLE 6. X-RAY DATA FOR $CaWO_4$ AND $CaMoO_4$

(The d values were derived from the measured 2θ values through the use of the tables of Ref. 10)

No.	Int. (obs.)	Natural Scheelite		Synthetic $CaWO_4$		Synthetic $CaMoO_4$	
		2θ (Cu)	d (Å)	2θ (Cu)	d (Å)	2θ (Cu)	d (Å)
1	6	18.82	4.72	18.86	4.71	18.87	4.71
2	4	26.04	3.42	26.10	3.41	26.11	3.41
3	10	29.01	3.08	28.96	3.08	29.00	3.08
4	4	34.42	2.605	34.39	2.608	34.48	2.601
5	4	39.41	2.286	39.39	2.287	39.59	2.276
6	3	42.50	2.127	42.55	2.125	42.49	2.128
7	1	43.48	2.081	43.53	2.082	—	—
8	1	44.29	2.045	44.37	2.042	44.42	2.041
9	3	45.60	1.989	45.65	1.987	45.79	1.982
10	8	47.30	1.923	47.32	1.921	47.34	1.920
11	6	49.31	1.848	49.33	1.847	49.54	1.840
12	4	52.10	1.755	52.04	1.757	52.18	1.753
13	1	53.40	1.716	53.28	1.719	53.57	1.711
14	4	54.48	1.684	54.52	1.683	54.42	1.686
15	2	56.60	1.626	56.53	1.626	56.46	1.630
16	9	58.05	1.589	58.07	1.588	58.06	1.589
17	8	59.71	1.549	59.68	1.549	59.75	1.545
18	4	64.91	1.437	64.94	1.436	65.00	1.435
19	4	67.80	1.382	67.84	1.382	67.83	1.382
20	4	69.34	1.355	69.54	1.355	69.59	1.351
21	4	70.64	1.333	70.64	1.333	70.73	1.332
22	2	72.30	1.309	72.24	1.308	72.57	1.303
23	2	75.29	1.262	75.36	1.261	—	—
24	9	76.41	1.247	76.41	1.247	76.32	1.248
25	1	78.16	1.223	78.07	1.224	—	—
26	6	79.52	1.205	79.55	1.205	79.80	1.202
27	6	80.86	1.1887	80.87	1.1886	81.07	1.1862
28	6	82.30	1.1715	82.40	1.1703	82.68	1.1671
29	1	86.19	1.1283	86.19	1.1283	86.08	1.1297
30	1	88.18	1.1080	88.25	1.1072	89.72	1.0927
31	8	90.76	1.0822	90.79	1.0819	91.00	1.0799
32	2	95.12	1.0437	95.02	1.0445	95.57	1.0400
33	2	96.51	1.0323	96.53	1.0322	96.47	1.0326
34	7	99.43	1.0097	99.41	1.0098	99.80	1.0070
35	2	—	—	100.86	.9992	—	—

TABLE 6 (*Continued*)

No.	Int. (obs.)	Natural Scheelite		Synthetic $CaWO_4$		Synthetic $CaMoO_4$	
		2θ (Cu)	d (Å)	2θ (Cu)	d (Å)	2θ (Cu)	d (Å)
36	2	106.22	.9631	106.29	.9626	106.22	.9631
37	2	108.16	.9511	108.17	.9511	108.44	.9493
38	2	—	—	110.61	.9368	110.30	.9386
39	8	117.02	.9033	116.99	.9034	117.24	.9022
40	6	120.41	.8876	120.41	.8876	121.05	.8848
41	6	122.05	.8805	122.00	.8807	122.59	.8782
42	3	—	—	127.38	.8593	—	—
43	5	131.90	.8435	131.86	.8436	131.90	.8435
44	6	134.68	.8347	134.70	.8346	135.20	.8331
45	6	136.64	.8289	136.67	.8288	137.27	.8271
46	8	142.99	.8122	142.96	.8123	143.50	.8110
47	3	—	—	—	—	150.64	.7962
48	9	150.91	.7958	150.90	.7958	152.06	.7937
49	8	152.13	.7936	152.10	.7937	153.26	.7917
50	3	162.24	.7796	162.19	.7796	164.68	.7772
51	8	165.53	.7764	165.54	.7764	166.22	.7759
52	5	167.98	.77450	167.98	.7745	168.85	.7739

All reflections with $2\theta > 90°$ are α_1 reflections.

by weight. Intermediate members of the scheelite-powellite series containing between 20 per cent and 80 per cent. $CaMoO_4$ are rare in nature, so that synthetic products had to be used in any case for those parts of the diagrams.

The x-ray diffraction angles for corresponding lines of natural scheelite and synthetic $CaWO_4$ are identical (see first two columns of Table 6), and it can, therefore, be inferred that the synthetic series will yield identical powder patterns to those of the minerals.

The diffraction angles for corresponding lines were found to increase in direct proportion to the $CaMoO_4$ content.

From Table 6 it is seen that the highest variations in 2θ are found in the high angle region, the higher the angle the larger the difference in 2θ. To establish the relationship between the variations of 2θ for corresponding lines in the spectra of different samples and the chemical composition, the lines marked 1, 2 and 3 in Fig. 3 were selected because they are:

(*a*) prominent and easily recognized,

(*b*) situated in the high angle region of the patterns where the accuracy of measurement is highest and the variation of 2θ is a maximum, and (*c*) the most intense and best defined back-reflection lines and unlikely to disappear when the sample is diluted with foreign material.

These three lines are identified as follows:

	Line No. 1	Line No. 2	Line No. 3
2θ (Cu)			
Scheelite	152.10°	150.90°	142.96°
Powellite	153.26°	152.06°	143.50°
d (Å)			
Scheelite	0.7937	0.7958	0.8123
Powellite	0.7917	0.7937	0.8111
Line No. in Table 6	49	48	46

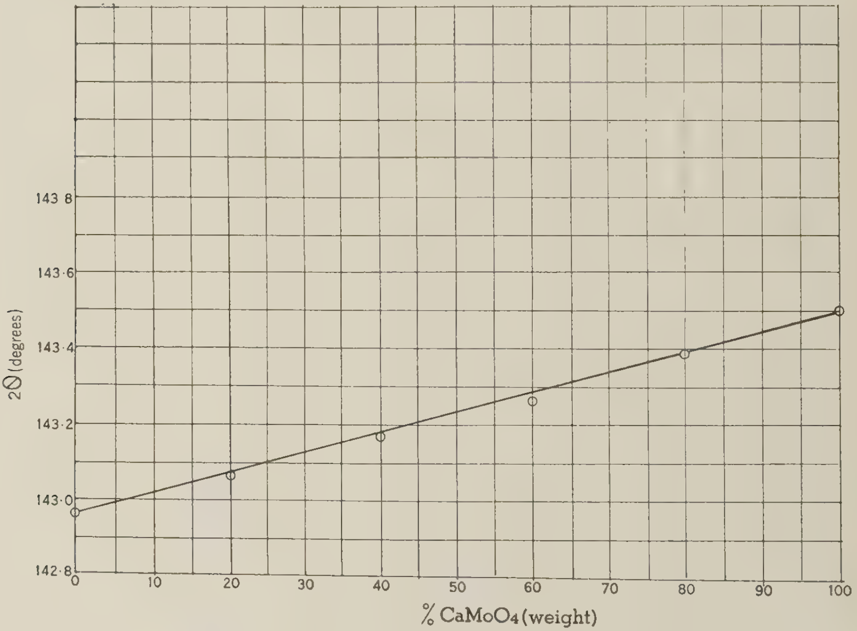

FIG. 6. Variation of 2θ for line No. 3 with the chemical composition in the scheelite-powellite series.

The three variation diagrams for different lines will suffice for practical purposes.

PRECISION

The values for 2θ are correct to 0.03 degrees, so that the diagrams represent the content of $CaMoO_4$ accurately to within 2 per cent. If all three lines used in the variation diagrams can be measured accurately, then the mean of these three values should give the MoO_3 content accurately to within 1 per cent.

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NEW OCCURRENCES OF MINERALS AT IRON MOUNTAIN, MISSOURI*

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ABSTRACT

Salite, actinolite, dolomite, and fluorite at Iron Mountain, Missouri, are reported for the first time. Salite, $Ca(Mg,Fe)(SiO_3)_2$, an intermediate pyroxene of the diopside-hedenbergite series, occurs as grayish-green columns up to 10 inches long in a skarn formed by the action of iron-bearing solutions on andesitic lava of pre-Cambrian age. It has the following chemical composition and optical properties: SiO_2, 52.76; Al_2O_3, 1.12; TiO_2, 0.16; Fe_2O_3, 1.73; FeO, 8.92; MnO, 0.47; CaO, 20.48; MgO, 13.43; Na_2O, 0.35; K_2O, 0.05; H_2O, 0.45; $\gamma=1.718$; $\beta=1.700$; $\alpha=1.691$; $2V=60°$; positive; $r>v$; $Z\wedge c=45°$; density $=3.350$. Locally salite was changed to actinolite, which has been called amphibole or tremolite; but optical properties of numerous grains fall within the range of actinolite with $\gamma=1.645$; $\alpha=1.625$; $Z\wedge c=15°$. The iron garnet, andradite ($N=1.88$), replaces actinolite; and euhedral, zoned dodecahedrons contain relict fibers of actinolite. Calcite, quartz, and hematite replace early minerals. Purple fluorite occurs in quartz, but it is not in contact with hematite so its age relation to hematite is uncertain. A pink carbonate the color of rhodochrosite occurs in veins cutting the andesitic lava, but it contains only 1.45 percent MnO and has the optical properties of dolomite with $\omega=1.685$. Thus, doubt is raised concerning the rhodochrosite and manganocalcite from this deposit that were reported in 1895.

INTRODUCTION

Extensive enlargement of the Hayes Cut in a specular hematite deposit at Iron Mountain, St. Francois County, Missouri, exposed additional outcrops of ore and the pre-Cambrian andesitic lava that forms the country rock. On August 1, 1950, the senior author collected four minerals there that had not been previously described in the Iron Mountain assemblage. These are salite, an intermediate pyroxene of the diopside-hedenbergite series; actinolite that had previously been called amphibole or tremolite; purple fluorite; and pink dolomite that has the color of rhodochrosite. On January 22, 1951, the senior author revisited both the Hayes Cut and the Big Cut with Joseph W. Fusso; and they found salite only in a restricted contact zone 1 to 10 inches wide in the new workings a few feet southeast of the old part of the Hayes Cut.

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PREVIOUS WORK

Hematite has been mined at Iron Mountain almost continuously from 1845 to the present. During this interval the total production of iron ore from the deposit has been reported to exceed 4,500,000 tons (Lake, 1932).

The geology of the deposit has been studied by Schmidt (1873), Nason (1892), Winslow, Haworth, and Nason (1894), Crane (1912), Spurr (1927), Singewald and Milton (1929), and Lake (1932).

Nason (1892, p. 51) considered the veins in porphyry as veins of infiltration, formed by replacement and precipitation when the waters are sufficiently saturated.

Crane (1912, p. 113) listed hematite, martite (slightly magnetic), quartz, amphibole (tremolite), and apatite as the vein minerals. He regarded the ore in part as a fissure filling but more largely as a replacement of porphyry.

Spurr (1927, p. 363) cited the deposit as an example of intrusive vein dikes of specular iron in porphyry.

Singewald and Milton (1929, p. 330) emphasized the fact that the ore bodies at Iron Mountain show replacement characteristics. They reported the mineral assemblage directly associated with the introduced hematite as quartz, apatite, garnet, tremolite, and calcite and regarded it as indicative of high-temperature mineralization.

Lake (1932, p. 56) stated that the primary ore consists principally of hematite with as much as 12 per cent of magnetite and small amounts of apatite and tremolite. Later minerals present in the ore are calcite, garnet, and quartz, which replace mainly the apatite and tremolite. He ascribed the ore to solution and stoping of the andesite porphyry by ore-bearing solutions.

OCCURRENCE AND PROPERTIES OF SALITE

Salite, a grayish-green pyroxene of the diopside-hedenbergite series, occurs as columns up to 10 inches long in a skarn formed by the action of iron-bearing solutions on andesitic lava of pre-Cambrian age now exposed in the Hayes Cut at Iron Mountain. Most of the material is contaminated with grains and stains of hematite and is unsatisfactory for chemical analysis. However, by careful hand-picking under a binocular microscope and rejecting fragments containing hematite impurities and by purifying with an electromagnet, a sample was prepared with less than one per cent hematite. This was analyzed by Joseph J. Fahey; the results are listed in Table 1. Joseph M. Axelrod of the U. S. Geological Survey made an *x*-ray diffraction pattern of this sample and reported it to be a monoclinic pyroxene with only a trace of hematite.

TABLE 1

	1	2	3
SiO_2	52.76	50.19	
Al_2O_3	1.12	2.73	
TiO_2	0.16	0.20	
Fe_2O_3	1.73	2.98	
FeO	8.92	7.54	
MnO	0.47	0.40	
CaO	20.48	23.58	
MgO	13.43	12.38	
Na_2O	0.35	0.45	
K_2O	0.05	0.00	
H_2O	0.45	0.02	
	99.92	100.47	
γ	1.718	1.7185	1.720
β	1.700	1.6980	1.697
α	1.691	1.6915	1.692
2V	60°	59°	56°
$Z\wedge c$	45°	45°	41°

No. 1. Salite from a skarn at the Hayes Cut at Iron Mountain, St. Francois County, Mo. Collected by V. T. Allen. J. J. Fahey, *analyst.*

No. 2. Salite from a skarn at the Clifton magnetite mine, St. Lawrence County, N. Y. Collected by B. F. Leonard. Norman Davidson, *analyst.* Optical properties by H. H. Hess. *Am. Mineral.*, **34**, 663 (1949).

No. 3. Optical data on salite from Iron Mountain, Mo., determined by H. H. Hess, using the same method as he did on No. 2. Data on salite from a similar but not the identical specimen No. 1. According to Hess it contains small inclusions or alterations.

Optically the salite from Iron Mountain, Missouri is positive, has indices of refraction $\gamma=1.718$, $\beta=1.700$; $\alpha=1.691$, $2V=60°$; $Z\wedge c=45°$; dispersion faint, $r>v$; pleochroism faint, none observable in thin section, X=Y=pale bluish green; Z=yellowish green. Density is 3.350. The optical properties, chemical composition, and occurrence of the salite at Iron Mountain are compared in Table 1 with those of salite from the Clifton magnetite mine, in St. Lawrence County, N. Y. Salite is a relatively rare mineral in the United States, but Hess (1949) has compiled four analyses of salite and three of ferrosalite from the anorthosite and magnetite regions of New York. Schmitt (1939) has reported salite from Hanover, New Mexico.

OCCURRENCE AND PROPERTIES OF ACTINOLITE

The fibrous gray amphibole at Iron Mountain has been called amphibole and tremolite, but the optical properties of numerous grains fall within the range of actinolite with $\gamma=1.645$, $\alpha=1.625$, $Z\wedge c=15°$. Attempts were made to prepare some of it for chemical analysis by handpicking and by using the electromagnet and heavy solutions, but hematite stains permeate all the material collected so that an accurate quantitative determination of the iron present as actinolite is impossible. Joseph M. Axelrod made *x*-ray diffraction patterns of the prepared samples and reported that they were the patterns of an amphibole containing several per cent of hematite as an impurity. Joseph J. Fahey determined the MnO on a typical sample of the actinolite from Iron Mountain to be 0.24 per cent. The possibility of the actinolite at Iron Mountain containing appreciable amounts of manganese and being related to winchite is thus removed. Also, the similarity to the amphibole at Thorny Mountain, Missouri, which gave a manganese bead test, is less striking than has been suggested (Grawe, 1943).

Occurrence of Fluorite and Dolomite

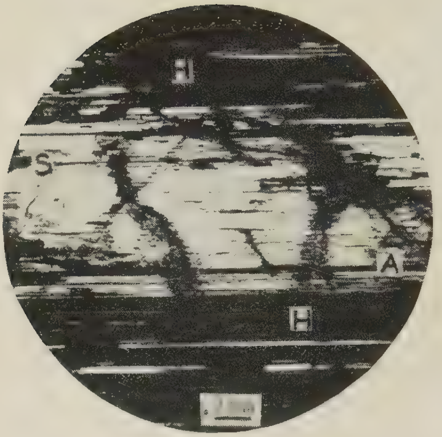
Purple fluorite with $N = 1.43$ occurs in quartz as granular masses 1 cm. or more long and about 0.5 cm. wide. It is not in contact with hematite, so its age relation to hematite is uncertain.

Pink dolomite fills veins up to ½ inch wide that cut the andesite porphyry. It has the color of rhodochrosite but has the optical properties of dolomite with $\omega = 1.685$. Joseph J. Fahey determined the manganese content of this pink carbonate as 1.45 per cent MnO. Wheeler (1895) reported rhodochrosite and manganocalcite filling seams in specular hematite at Iron Mountain. He named W. B. Potter as the collector, but did not give the evidence on which the determination was made. The pink dolomite with 1.45 per cent MnO shows that color is unreliable as a diagnostic property of rhodochrosite. The validity of this reported occurrence of rhodochrosite and manganocalcite is questionable.

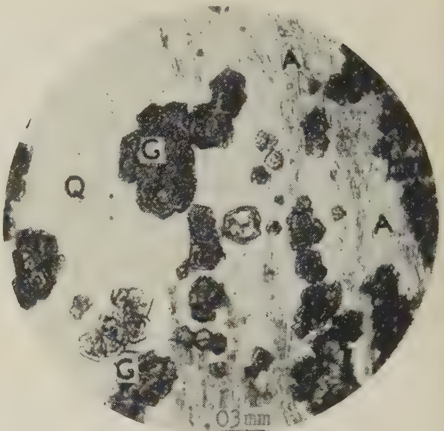
Origin and Sequence of Minerals

Salite, $Ca(Mg,Fe)(SiO_3)_2$, was formed by hot iron-bearing solutions that arose along fissures and attacked the andesitic lava at Iron Mountain. Salite occurs in contact with the andesite porphyry, and stout columns up to 10 inches long project from the wall rock into the ore.

As the temperature of the iron-bearing solutions decreased salite was locally changed to actinolite, $Ca\ (Mg,Fe)_5\ (OH)_2(Si_4O_{11})_2$. Specimens are present in which the columnar structure of salite grades into the fibrous habit of actinolite. Small relict areas of salite that have the extinction angle and indices of refraction of salite persist locally in the actinolite, but in most of the commercial ore the change to actinolite is complete. Apparently, one area southeast of the old part of the Hayes Cut escaped the effect of this later alteration, for there large columns of salite remain unaltered. At many places at Iron Mountain the composition of the lava



(a)



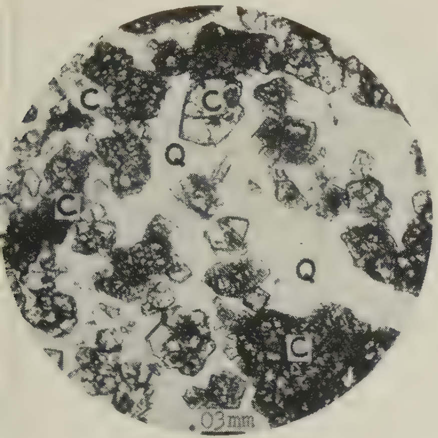
(b)

FIG. 1*a*. Salite (*S*) is altered to actinolite (*A*). Hematite (*H*, black) replaces actinolite and salite along cracks and cleavage. In other thin sections remnants of salite remain in some of the actinolite.

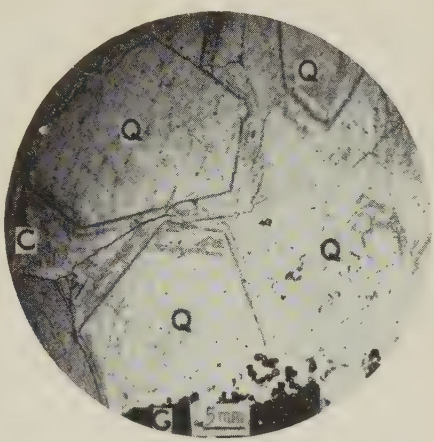
FIG. 1*b*. Zoned garnets (*G*) replace actinolite needles (*A*) and contain relict needles of actinolite. White (*Q*) is quartz.

series and the conditions of crystallization favored the formation of epidote, $HCa_2(Al,Fe)_3\ Si_3O_{13}$, without any trace of salite or actinolite. In the Big Cut at Iron Mountain, epidote is the characteristic mineral associated with the ore.

The iron garnet andradite, $(Ca_3Fe_2)(SiO_4)_3$, is present as euhedral, zoned dodecahedrons that cut across the actinolite and contain fibrous inclusions of actinolite (Fig. 1*b*). The zoned andradite is birefringent and has an index of refraction of 1.88. The determination of the temperature at which birefringent garnets become isotropic by heating has been used to indicate the temperature below which the garnet crystallized. Merwin (1915) found that contact garnets from Alaska lost their birefringence when they were heated to about 800° C. Stose and Glass (1938) determined 860° C. as the temperature at which zoned birefringent andradite from Pennsylvania became isotropic. Ingerson and Barksdale (1943) observed that in an iridescent garnet from Nevada the birefringence did not decrease until the temperature reached 1060° C. and continued practically to the melting point. If the garnet at Iron Mountain actually crystallized after the hematite as Lake (1932, p. 58) suggested, the loss of birefringence of the garnet at Iron Mountain could be used to fix the temperature above which the associated specular hematite was formed. But, the opinion of Singewald and Milton (1929) that garnet at Iron Mountain tends to be earlier than hematite, and is replaced by it is supported by several specimens studied during this investigation in



(a)



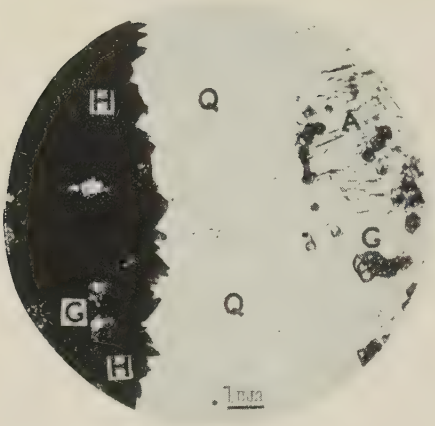
(b)

FIG. 2*a*. Garnet is replaced by calcite (*C*). White (*Q*) is quartz.
FIG. 2*b*. Prismatic quartz (*Q*), calcite (*C*), garnet (*G*).

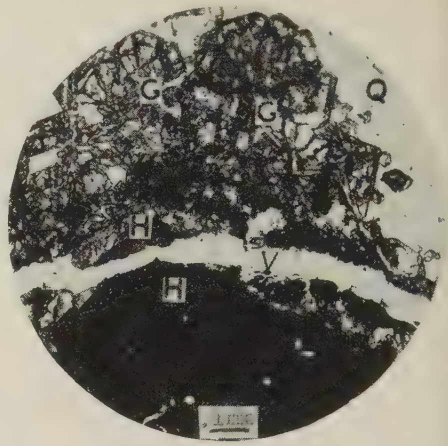
which garnet is cut by and replaced by hematite. In the light of the work of several investigators on the loss of birefringence of garnets, a temperature below 800° C. is suggested for the formation of specular hematite at the Iron Mountain deposit.

Calcite replaces garnet (Fig. 2*a*) and the centers of garnet crystals are occupied by calcite that entered through channels cutting the rim. The replacement of early minerals by calcite at Iron Mountain produces unusual effects in thin section. In some of the calcite replacing early minerals the color is brown, almost the brown of siderite, but the indices of refraction are within the range of those for calcite.

Quartz occurs as prismatic crystals in the ore (Fig. 2*b*). It also fills cracks or veins cutting hematite, garnet, and the early minerals (Fig. 3*b*). The period of quartz deposition was probably long and overlapped the formation of hematite. Terminated crystals of hematite that suggest growth in an open cavity are in contact with quartz (Fig. 3*a*), but veins of quartz also cut hematite and garnet in the same specimen (Fig. 3*b*). Some of the quartz replacing other minerals has a peculiar tan to brown color. Other quartz contains myriads of needles of actinolite that are oriented parallel to the adjacent actinolite (Fig. 1*b*) and portray convincing evidence of replacement. Likewise hematite penetrates and replaces salite along cracks and cleavage (Fig. 1*a*) and permeates and replaces the actinolite so thoroughly that even the smallest needle is contaminated with it. The color of the cleavage surfaces of some actinolite has been changed to reddish brown by hematite that has impregnated it. Chlorite is associated with the hematite in thin section and probably accom-



(a)



(b)

Fig. 3*a*. Terminated crystals of hematite (*H*, black) suggest growth in a cavity. Later quartz (*Q*) filled the cavity. Actinolite (*A*) and garnet (*G*) are cut by quartz (*Q*).

Fig. 3*b*. Quartz vein (*V*) cuts hematite (*H*) and garnet (*G*).

panied its introduction. Apatite reported by other observers at Iron Mountain is absent from the thin sections and specimens studied during this investigation. Fluorite occupies the center of massive quartz in a vein an inch wide and appears to be the last mineral to form. The sequence of minerals extending in each direction perpendicular to the center of the vein includes fluorite, quartz, calcite of white and brownish color, garnet, hematite, and actinolite.

Table 2. Sequence of Minerals at Iron Mountain, Missouri

Salite, $Ca(Mg,Fe)(SiO_3)_2$	——				
Actinolite, $Ca_2(Mg,Fe)_5(OH)_2(Si_4O_{11})_2$		——			
Andradite, $(Ca_3,Fe_2)(SiO_4)_3$			——		
Hematite, Fe_2O_3				——	
Calcite, $CaCO_3$				———	
Quartz, SiO_2				—————	
Fluorite, CaF_2					——

Conclusions

Salite was the first mineral to be formed from the andesite porphyry by the iron-bearing solutions at Iron Mountain, Missouri. In most of the commercial ore the salite is absent and its place is taken by actinolite or epidote. Andradite, calcite, quartz and specular hematite replace the early minerals and the andesite porphyry. The mineral sequence suggests that magnesia was removed first from the ore-bearing solutions and was fixed as salite and actinolite crystallized. After the deposition of andradite at some places and epidote at others, the temperature was favorable and sufficient carbon dioxide was present in the system to utilize most of the calcium to form calcite. This liberated iron to form hematite and silica to form quartz and concentrated fluorine and calcium to form fluorite.

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The writers are grateful to Mr. Joseph W. Fusso for his help and for the specimens that he contributed to this investigation. The *x*-ray determinations by Joseph M. Axelrod and his estimates of the amount of hematite in the samples of actinolite and pyroxene prepared for chemical analyses are gratefully acknowledged. Appreciation is expressed to the resident staff members of the Ozark Ore Company for courtesies extended during several visits to their property, and to Professor H. H. Hess for checking the birefringence and indices of refraction of a specimen of salite from Iron Mountain.

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A TEST OF THE ACCURACY OF CHEMICAL ANALYSIS OF SILICATE ROCKS

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Abstract

A six-component silicate glass of the proportions found in granite was prepared and its composition controlled so that significant errors were eliminated except for SiO_2 (.02%) and Al_2O_3 (.01%). Analysis of this glass by eleven chemical laboratories gave mean values which showed satisfactory agreement ($<.1\%$) for MgO, CaO, Na_2O, K_2O. For SiO_2 and Al_2O_3 a reciprocal systematic error appeared whereby SiO_2 was .4% low and Al_2O_3 was .6% high; total SiO_2 and Al_2O_3 agreed almost exactly ($<.1\%$) with the glass standard. The practical problem of evaluating error in a single analysis is discussed briefly in its relation to these results.

Introduction

The need for reliable standards in spectrochemical analysis of the major elements of silicate rocks led recently to a chemical study of the composition of two provisional standards (*G-1*, a granite from Westerly, R. I.; *W-1*, a diabase from Centerville, Va.). With the co-operation of twenty-four laboratories from various parts of the world, data on these two rocks were assembled and means computed for all the major elements. This work, together with an investigation of the minor elements and a study of the modal composition of the granite, has been recently published (1).

Although a majority of the chemical determinations were closely grouped about a central consensus value, the over-all dispersion for a number of elements was disturbingly large and it was suggested (1) that, if a synthetic silicate mixture could be obtained, a second round of analyses on this new material of *known* composition might be illuminating. In other words, whereas the original investigation was a test of analytical precision, the second one would test accuracy as well. So far as we are aware, no check of this kind has ever been carried out to test the various procedures used in silicate analysis. Through the co-operation of a number of organizations and individuals, acknowledged elsewhere in this paper, we are now able to report on this matter and to comment on its relation to the previous work.

Preparation of the Standard

A composition for the standard was selected which would closely approximate the granite *G-1* already analyzed. This would tend to maintain precision of analysis at the same level as for *G-1* and thus simplify interpretation of the results. The following composition was decided on:

Norm		*Composition (Wt. %)*	
Q	27.0	SiO_2	72.64
Cor	1.0	Al_2O_3	15.78
Or	34.0	CaO	1.82
Ab	27.0	MgO	0.80
An	9.0	K_2O	5.76
En	2.0	Na_2O	3.19
Sum	100.0	Sum	99.99

A silicate mixture of this kind may be termed a haplogranite, following Bowen's nomenclature.* No iron was deliberately added, although a small amount is present (as Fe_2O_3) in the final product through contamination from steel mortars. Similarly, a small amount of platinum is present because of preparation in platinum crucibles. The MgO content is slightly higher than in many granites but no higher than in some biotite or pyroxene granites. The value for MgO was deliberately selected to lower viscosity of the melt and thereby reduce the labor of preparation.

The sample was prepared at the Geophysical Laboratory† using materials and procedures which have been standard there for many years. As a source of potash, potassium tetrasilicate glass ($K_2O \cdot 4SiO_2$) was prepared in a platinum crucible from purified quartz (residue after treatment with HF and H_2SO_4, 0.03%) and chemically pure $KHCO_3$ (Baker & Adamson, lot No. 3772). If these materials are first sintered at 700° C., and the temperature is then raised very gradually over a period of several days, the K_2O loss after complete fusion at 1200° C. is negligible. The loss of K_2O from 20.0000 gms. of $K_2O \cdot 4SiO_2$ glass was 0.0013 gm. This small loss was replaced and the glass fused three times at 1200°, with intermediate crushing, to yield a homogeneous glass which was crystallized completely at 700° C. to pure crystalline $K_2O \cdot 4SiO_2$. This remained dry in a desiccator over fused KOH sticks and could easily be weighed on a watch glass. Similarly, as a source of Na_2O, sodium disilicate glass ($Na_2O \cdot 2SiO_2$) was prepared from the same purified quartz and from chemically pure anhydrous Na_2CO_3 (prepared by heating $NaHCO_3$, Merck & Co., lot No. 42584, at 350° C.). During the preparation of $Na_2O \cdot 2SiO_2$ the loss before correction on a 20.0000 gm. batch after the complete fusion at 1200° C. was only 0.0019 gm. Crystalline $Na_2O \cdot 2SiO_2$ remains dry in a desiccator over fused KOH sticks and can easily be weighed on a watch glass.

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* The term haplobasaltic was used by N. L. Bowen (*Am. Jour. Sci.*, **40**, 161–185, 1915) for compositions approaching the composition of basalt, *i.e.*, a simplified basalt. In an analogous way we use the term haplogranite.

† J. F. Schairer prepared the sample, assisted by Robert D. Thwaite.

To provide the proper amounts of SiO_2, Al_2O_3, CaO, and MgO to yield the desired haplogranite composition when mixed with the appropriate amounts of $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$, a "haploresidue" glass was prepared. This had the composition SiO_2 73.778%, Al_2O_3 22.489%, CaO 2.594%, and MgO 1.140%. Three 25-gram batches of the "haploresidue" glass were prepared from the purified quartz, tabular Al_2O_3 (T61, Aluminum Company of America), C. P. MgO (J. P. Baker & Co., lot. No. 82735), C. P. $CaCO_3$ (Baker & Adamson, C. P. Special). Each batch was fused six times at 1600° C. with intermediate crushing in a steel mortar and removal of steel particles magnetically. Although the resulting glass was uniform in composition (as shown by refractive index tests), small, evenly distributed laths of mullite were present because of the very high liquidus temperature of this composition. After drying for eighteen hours at 900° C., the powdered glass remained dry in a desiccator over fused KOH sticks and could be weighed readily into a platinum crucible.

Four 25-gram batches of haplogranite were prepared in platinum crucibles from the three ingredients whose preparation has just been described. Each batch was fused six times at 1520° C. with intermediate crushing in a steel mortar and removal of steel magnetically. Finally, the four batches were combined in one large platinum crucible and fused at 1200° C. four times with intermediate rough crushing (without use of a steel mortar) to insure thorough mixing of the four batches. Optical examination of the final glass showed a uniform index of refraction 1.491.

The final glass was crushed in a large steel mortar to pass 80-mesh bolting cloth; no metallic sieves were used. Great care was taken to avoid any rotation of the pestle during crushing which might produce a smear of steel on the glass powder. A small amount that would not crush fine in this mortar was rejected. To avoid excessive platinum contamination no attempt was made to remove all glass from the large crucible. Despite these losses and others inherent in each crushing operation, a 92-gram sample of the haplogranite was obtained.

As stated above, no iron was deliberately added in the preparation of the haplogranite. Small amounts, however, are unavoidably introduced by the numerous crushings in a steel mortar even though great care was taken to remove as many as possible of the tiny steel fragments with a magnet after each crushing. The residual iron was oxidized to Fe_2O_3 and dissolved in the melt. On the basis of past experience it might be expected that at least 0.1%, and possibly (though not likely) as much as 0.3% of Fe_2O_3 is present because of this unavoidable contamination during crushing operations.

Reliability of the Composition

It is obviously important to list and assess all possible sources of error in preparation of the haplogranite glass. These are of two kinds: (1) errors arising from impurities in the original ingredients and of the intermediate products, and (2) errors arising from processing of the ingredients. Tables 1 and 2 summarize and evaluate these types of error.

Ingredients

Errors arising from impurities in the ingredients are significant only for SiO_2 and Al_2O_3, quantitatively the two principal constituents of the glass. The quartz used as a source of the SiO_2 is a very pure vein material obtained a number of years ago from Lisbon, Maryland. Several hundred pounds of selected fragments were crushed in a ball mill (using steel balls), treated with hot dilute HCl, then washed and dried. A 10-gram sample of this material treated with H_2SO_4 and HF left an insoluble residue of only .03%.

Table 1. Errors in the Glass Composition Arising from Impurities in the Original Ingredients

Ingredient	Impurity		Estimated Resultant Error		
	Amount	Nature of Impurity	Constituent	Amount	Remarks
Quartz	.03%	Insoluble residue	SiO_2	.02%	Deficiency
Alumina	.075%	(SiO_2 .02, Na_2O .02, Fe_2O_3 .03, TiO_2 .005)	Al_2O_3	.01%	Deficiency
Magnesia	.02%	Alkalis, mostly Na_2O	MgO	.00×%	Negligible
Calcium carbonate	.03%	Alkalis	CaO	.000×%	Negligible
Sodium bicarbonate	.037%	Insoluble .015 CaO+MgO .002 Fe .020	Na_2O	.00×%	Negligible
Potassium bicarbonate	.005%	SiO_2 .003, Al_2O_3+ Fe_2O_3 .001, CaO .001	K_2O	.000×%	Negligible
			Total	.03%	Deficiency

The alumina (Tabular Alumina T-61, Aluminum Company of America) has impurities as listed in the table. The SiO_2 impurity in the alumina will replace a small part of the SiO_2 deficiency of the quartz, but not by a significant amount (only .003% proportionately). Likewise the amount of Na_2O is too small (∼.003% proportionately) to make any significant change in the over-all amount of Na_2O in the haplogranite glass. The Fe_2O_3 and TiO_2 impurities (.006% proportionately) will appear as a minor part of the total Fe_2O_3 unavoidably added to the glass by grinding in steel mortars (Table 3).

The magnesia has a much greater proportion of impurity than the other ingredients (.20% alkalis, mostly Na_2O,) but because of the small amount required in preparation of the haglogranite glass the proportion of alkalis added is negligible.

Calcium carbonate, the source of CaO, is a highly purified compound (Baker & Adamson, C. P. Special). A careful alkali determination made at the Geophysical Laboratory showed .03% total alkalis in a 5-gram sample.* The net impurity added to the haplogranite from this source is obviously negligible. The sodium and potassium bicarbonates used to prepare the intermediate products $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$ were C. P. grade and contained the impurities noted in the table. No significant contribution to the total error in the haplogranite composition was made by either of these two ingredients.

Processing of Ingredients

Table 2 subdivides errors arising from preparation of the haplogranite glass into three groups. The first of these is considered negligible for the reason noted in the table. The second concerns volatilization losses in synthesizing $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$. The precautions taken to avoid these losses have already been stated. The losses, .0013 gm. K_2O and .0019 gm. Na_2O, are in themselves negligible, but were nevertheless replaced.†

The next source of error stems from crushing and grinding operations. Loss of fines, at any stage of preparation where the glass is still inhomogeneous, could be a serious source of error. As indicated in the table and already mentioned in the preceding section, precautions were taken which it is believed have avoided any significant error from this source.

Contamination of the glass by fusion in platinum crucibles and grinding in steel mortars is a significant and unavoidable source of error. Table 3 gives the available data for Fe_2O_3. The laboratories not listed made no separate determination of Fe_2O_3 from their R_2O_3 precipitates. Omitting the result from Laboratory 8, which statistically as well as by later admission of the analyst is improbable, a mean of .15% Fe_2O_3 is the best

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* $CaSiO_3$ made from this $CaCO_3$ provides a standard for calibration of thermocouples at the Geophysical Laboratory, since its freedom from significant impurities gives it an unusually small melting interval of .75° C.

† Further evidence that loss of alkalis can be controlled and eliminated comes from crystallization studies of glasses of feldspar composition. New hydrothermal techniques now make possible rapid crystallization and it is found that such glasses crystallize completely to feldspar, with no evidence of residual glass or additional crystal phases.

TABLE 2. ERRORS IN THE GLASS COMPOSITION ARISING FROM PROCESSING OF ORIGINAL INGREDIENTS AND OF INTERMEDIATE PRODUCTS

Source of Error	Evaluation
Weighing	*Negligible*, in view of .000× uncertainty in individual weighings and relatively large sample size. (The smallest weighing was 0.2850.)
Volatilization of Alkalis	.0013 gm. loss in K_2O from preparation of 20.0000 gm. sample of $K_2O \cdot 4SiO_2$. .0019 gm. loss in Na_2O from preparation of 20.0000 gm. sample of $Na_2O \cdot 2SiO_2$. These losses were replaced and error from volatilization is believed to be *negligible*.
Crushing and Grinding 1. Loss of Fines	Unknown losses, but could lead to significant error only after the *first* fusion when glass is relatively inhomogeneous. Fine grinding was avoided at this stage and error is believed to be *negligible*.
2. Contamination by Containers	.15% Fe_2O_3 is the estimate of contamination by steel mortars .10% *Pt* is the estimate of contamination by platinum crucibles.
Adsorption of Water by Glass Powder	.08% H_2O is the preferred estimate of error arising from adsorption.

TABLE 3. DATA ON Fe_2O_3 IN THE HAPLOGRANITE GLASS

Laboratory	Wt. %	Remarks
3	.20	
4	.16	Analyst made careful determination with an independent sample.
6	.12	
8	.32	Analyst later reported that this value was probably too high.
10	.16	Average of .16 and .17.
11	.07	Reported as .05 Fe.
12	.17	Average of .14, .16, .20 by three analysts. Each analyst made triplicate determinations.
Average (omitting Laboratory 8)	.15	

available estimate of iron contamination and is entirely in line with the past experience at the Geophysical Laboratory.

A platinum content of .10% was determined by Laboratory 10, which would appear to be a reasonable estimate of view in the repeated fusions carried out in platinum crucibles.

Adsorption of water by the finely ground glass is to be expected and the available data are summarized in Table 4. Because of the low concentration of adsorbed water, agreement is poor and one result (Laboratory 1) may be considered improbable. However, as the correction for water is small relative to that for Fe_2O_3, it makes little difference whether or not the estimate of .08 is off by one or more digits.

TABLE 4. DATA ON H_2O+ IN THE HAPLOGRANITE GLASS

Laboratory	Wt. %	Remarks
1	.00	Improbable
2	.08	
3	.01	
4	.14	
6	.14	
7	.08	Analyst reported two determinations, each .08%.
8	.08	
9	.05	
11	.12	
12	.05	Average of .05, .03, .06 by three analysts, each making triplicate determinations.
Average (omitting Laboratory 1)	.08	

In summary, the composition of the glass as given shows a deficiency of .02% SiO_2, .01% Al_2O_3; in addition it contains .15% Fe_2O_3, .10% Pt., .08% H_2O. Considering also possible "handling" errors, loss of fines by grinding before homogenization of the glass, etc., it is nevertheless believed that at worst each value given for the synthetic rock is correct in the first decimal place, with small uncertainties in the second.

SELECTION OF ANALYSTS

As only a limited amount of the synthetic standard was available, the test had to be on a smaller scale than its predecessor. It was desirable in general to have the same laboratories, and, if possible, the same analysts, carry out the work. With one or two exceptions this was done. The selection of the laboratories and analysts listed under "Acknowledgments" was based on the nearness of their determinations in *G-1* and *W-1* to the mean values. The selection was somewhat arbitrary, for two reasons:

(1) the mean value is assumed to be an unbiased estimate of the correct value, which may or may not be true; and (2) certain analysts approached the mean very closely for some constituents and were wide of this mark for others. Real uncertainty arose, therefore, in several instances as to which would probably have given essentially the same data. Each analyst was provided with 3 grams of the standard; small additional quantities were supplied if requested.

RESULTS OF THE TEST

Table 5 shows the analyses of the glass as reported by twelve laboratories. Table 6 shows the analyses after alterations have been made as follows:

(1) .15% Fe_2O_3 is deducted from Al_2O_3 if no Fe_2O_3 was reported by the analyst (see Table 3 for data on Fe_2O_3).

(2) .08% H_2O+ is added to the analysis if none was reported (see Table 4 for data on H_2O).

TABLE 5. DATA ON GLASS AS REPORTED BY ANALYSTS

Laboratory*	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	H_2O+	H_2O-	Total
1	72.06	16.30		.88	2.04	3.81	5.38	.00		100.47
2	72.08	15.93		.87	1.83	3.34	5.70	.08	.10	99.93
3	71.69	16.71	.20	.75	1.91	3.14	5.74	<.01	.12	100.27
4	72.06	16.32	.16	.90	1.66	3.24	5.55	.14	.02	100.05
5	72.18	16.22		.82	1.88	3.07	5.68			99.85
6	72.49	16.06	.12	.81	1.84	3.12	5.63	.14†		100.21
7	72.02	16.36		.82	1.99	3.06	5.74	.08		100.06
8	72.00	16.27	.32	.88	1.99	3.10	5.60	.08	.01	100.25
9	71.90	16.01	tr.	.89	2.34	3.26	5.73	.05	.00	100.28
10	72.06	15.92	.19	.86	1.89	3.26	5.77			99.95
11	71.11	16.15	.07‡	.86	1.89	3.13	5.82	.12	.08	99.16
12	72.47	15.59	.14	.84	1.79	3.22	5.60	.05		99.70
	72.51	15.70	.20	.88	1.80	3.04	5.62	.03		99.78
	72.28	15.92	.16	.87	1.84	3.15	5.64	.06		99.92

* In the same order, these laboratories are numbered 17, 19, 25, 8, 13, 12, 10, 34, 20 7, 23, in the earlier test (1).

† Reported as ignition loss.

‡ Analyst reported .05 Fe.

TABLE 6. DATA ON SYNTHETIC GRANITE GLASS—Recalculated for Comparison with the Standard Composition

Laboratory	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	$SiO_2+Al_2O_3$	Total
1	72.30	16.20	.88	2.05	3.82*	5.40*	88.50	100.65
2	72.40	15.85	.87	1.84	3.35	5.72	88.25	100.03
3	72.01	16.78*	.75*	1.92	3.15	5.76	88.79	100.37
4	72.37	16.39	.90	1.67	3.25	5.57	88.76	100.15
5	72.42	16.12	.82	1.89	3.08	5.70	88.54	100.03
6	72.75	16.12	.81	1.85	3.13	5.65	88.87	100.31
7	72.25	16.27	.82	1.99	3.07	5.76	88.52	100.16
8	72.24	16.34	.88	2.00	3.11	5.62	88.58	100.19
9	72.11	15.91	.89	2.35	3.27	5.75	88.02	100.28
10	72.35	15.98	.86	1.90	3.27	5.79	88.33	100.15
11	71.38*	16.14	.86	1.90	3.14	5.84	87.52	99.26
$\bar{x}$	*72.23*	*16.19*	*.85*	*1.94*	*3.24*	*5.69*	*88.42*	*100.15*
$s_{\bar{x}}$	.10	.08	.01	.05	.06	.04	.11	.09
E	.1	.5	1.6	2.6	2.0	.7	.1	.9
s	.34	.26	.05	.17	.21	.12	.36	.31
C	.5	1.6	5.4	8.7	6.5	2.2	.4	.3
12	72.69	15.64	.84	1.79	3.23	5.61	88.33	99.80
(Not included	72.75	15.75	.88	1.81	3.05	5.64	88.50	99.88
in above	72.51	15.97	.87	1.85	3.16	5.66	88.48	100.02
average)								
Mean for Lab. 12	*72.65*	*15.79*	*.86*	*1.82*	*3.15*	*5.64*	*88.44*	*99.91*
Standard Composition	*72.64*	*15.78*	*.80*	*1.82*	*3.19*	*5.76*	*88.42*	*99.99*

Symbols: $\bar{x}$ arith. mean
s standard deviation } for single
C % relative deviation } determinations
$s_{\bar{x}}$ standard error } for the mean
E % relative error } for the mean

Analyses based on Fe_2O_3 = .15
H_2O+ = .08
Pt = .10
as the best estimate of unavoidable impurities. Each analysis recalculated in terms of SiO_2, Al_2O_3, MgO, CaO, Na_2O, K_2O only.

* Values which differ from the mean $\bar{x}$ by more than $2s$.

(3) .10% Pt is added to each analysis.

(4) A new summation is made which includes Fe_2O_3, Pt, H_2O+.

(5) Using this revised summation the glass composition is then recalculated omitting Fe_2O_3, H_2O+, H_2O-, and Pt.

The above alterations permit direct comparison of the analyses with the standard composition. In compiling the table Laboratory 12 is not included in the calculation of mean values as it did not participate in the original tests on *G-1* and *W-1.*

At the outset it need hardly be said that all the analytical work was done without foreknowledge of the composition of the glass. The nature of the test was, however, made known to each laboratory and presumably better-than-routine work was accomplished.

Precision

Data on precision of the test are included in Table 6. The standard deviation s, standard error $s_{\bar{x}}$, and their per cent equivalents, C and E respectively, are of the same order of magnitude as calculated for these laboratories in the previous test on the two rock samples *G-1* and *W-1.* Table 7 is a comparison with *G-1.* With one exception relative precision increases regularly with concentration of constituent. The exception, MgO, shows higher precision than might be expected. This stems at least in part from its higher concentration in the glass than in *G-1* and in any case need cause no concern.

TABLE 7. COMPARISON OF PRECISION OF ANALYSIS OBTAINED FOR HAPLOGRANITE GLASS AND G-1

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O
Glass $\bar{x}$	72.23	16.19	.85	1.94	3.24	5.69
$s_{\bar{x}}$	.10	.08	.01	.05	.06	.04
E	.1	.5	1.6	2.6	2.0	.7
G-1 $\bar{x}$	72.42	14.42	.39	1.38	3.30	5.52
$s_{\bar{x}}$	.08	.06	.02	.03	.04	.05
E	.1	.4	6.1	2.5	1.5	1.0

Accuracy

Since the level of precision is closely comparable with the previous test on *G-1*, the quite different matter of accuracy can now be fairly assessed. Inspection of Table 6 shows differences between standard and analytical (mean) values of somewhat less than 0.1% for MgO, CaO, Na_2O, and K_2O. Lacking evidence to the contrary, these differences may be attributed either to experimental error, or to the relatively small number of determinations made. For SiO_2 and Al_2O_3, however, a systematic discrepancy appears in the data for Laboratories 1 to 11, whereby the analytical means for SiO_2 and Al_2O_3 are 0.4% low and 0.6% high, respectively. The sum, $SiO_2+Al_2O_3$, however, agrees with the known composition almost exactly. If values for each constituent which differ from the mean by more than 2*s* are discarded, the revised means for Na_2O, CaO, K_2O change in the direction of the standard value; the new mean alters the difference from the standard from .4 to .5 for SiO_2 and for Al_2O_3 from .6 to .5. The changes for CaO, Na_2O, K_2O are all in a direction which indicates that the discarded values are erroneous; as will be indicated in the next paragraph, this also holds for SiO_2 and Al_2O_3.

The reciprocal low and high values for SiO_2 and Al_2O_3, respectively, form an aspect of the investigation which was quite unforeseen. Since the trend of these discrepancies corresponds with a recognized direction of analytical error, the test indicates that this type of systematic error still remains and has been inadequately investigated by the majority of silicate rock analysts. The discrepancies cannot stem from imperfections in the standard,* since the $Al_2O_3+SiO_2$ totals agree too closely. Laboratory 12 obtained excellent agreement with each of SiO_2 and Al_2O_3, as well as with the total. Since individual analyses in Table 6 vary between 0.1% and 0.9% low for SiO_2 and between 0% and 1% high for Al_2O_3, it becomes an important matter to review the procedures which have led to these aberrations. Several laboratories are now engaged with this and may report on it at a later time.

If it is assumed that the systematic error in SiO_2 and Al_2O_3 can be removed and that these values can be made to match as closely as for the other constituents, it may then be said that the test of accuracy has been squarely met by the analysts and the specter of systematic error laid low. A qualifying statement must follow, however, that the test compares *mean* values only. As a practical matter, for reasons both of time and expense, few rock samples are ever subjected to more than *one* chemical analysis, and, whatever the problem, the matter of accuracy usually stands or falls on the merits of the single analysis. This is, of course, the same problem which arose in the more comprehensive test on the provisional standards *G-1* and *W-1* (1) except for the fact that no standard of accuracy could there be applied. In the present test where an accuracy standard is available, and there is satisfactory agreement between the analytic mean and the standard values, the purely statistical approach would point to the standard deviation as a measure of the error of a single analysis. That is, based on a mean of 11 determinations, only one out of three determinations is likely to deviate from the mean by more than the number representing *s*. Since for MgO, Na_2O, K_2O the difference between the composition of the standard and the analytic means is much

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* Even if one applies to the glass standard the estimated errors in SiO_2 (.02) and Al_2O_3 (.01) (Table 1), the maximum range in values for these constituents will not significantly alter this conclusion.

TABLE 8. NORMS FOR SYNTHETIC GRANITE GLASS

Laboratory	Quartz	Corundum	Orthoclase	Albite	Anorthite	Enstatite
1	23.4*	.3	31.9*	32.2*	10.1	2.2
2	25.5	.8	33.8	28.3	9.1	2.2
3	26.1	1.8	34.0	26.6	9.5	1.9*
4	27.0	2.0	32.9	27.4	8.3	2.2
5	27.1	1.4	33.7	26.0	9.4	2.0
6	27.4	1.5	33.4	26.5	9.2	2.0
7	26.6	1.3	34.0	25.9	9.9	2.0
8	26.7	1.5	33.3	26.3	9.9	2.2
9	24.5	0*	34.0	27.6	11.6*	2.2
10	25.5	.9	34.2	27.6	9.4	2.1
11	25.1	1.2	34.5	26.5	9.4	2.1
$\bar{x}$	*25.9*	*1.2*	*33.6*	*27.4*	*9.6*	*2.1*
$s_{\bar{x}}$	.4	.2	.2	.5	.2	.03
E	1.4	15.4	.6	2.0	2.6	1.6
s	1.2	.6	.7	1.8	.8	.1
C	4.8	50.8	2.2	6.6	8.5	5.2
Lab. 12 Norm	*27.3*	*1.2*	*33.4*	*26.6*	*9.0*	*2.1*
Standard Norm	*27.0*	*1.0*	*34.0*	*27.0*	*9.0*	*2.0*

Symbols: $\bar{x}$ arith. mean
s standard deviation } for single determinations
C % relative deviation } for single determinations
$s_{\bar{x}}$ standard error } for the mean
E % relative error } for the mean
* Values which differ from the mean by more than 2s.

Classification of Glass
Class I
Order 4
Rang 2
Sub-rang 3

less than the standard deviation (CaO excepted), a reasonable estimate of the true value is given by the majority of the individual determinations where s is known. This is not true of the values with an asterisk in Table 6, each of which differs from its mean by more than $2s$. Unfortunately, even with a selected group of laboratories aware of the nature of the test, one determination in each column has an asterisk and so fails to measure up to the statistical standard. That is, about 10% of the determinations are of doubtful value. Routine work and less experienced analysts would undoubtedly have produced a larger percentage of improbable results. It should also be noted that the analysts responsible for the $>2s$ determinations in Table 6 were well within the $2s$ limit for these same constituents in *G-1* and *W-1*. There is thus no unique way to evaluate error in the components of a single analysis. The best compromise would be frequent checking by the analyst on his ability to approach the mean values obtained for *G-1* and *W-1* (1). A revised set of means for these standards* will be available shortly; these will be based on the later results of this investigation and on additional analyses of *G-1* and *W-1*.

Summarizing these results, the accuracy obtainable with present analytical procedures for MgO, CaO, Na_2O, K_2O is satisfactory; additional research is needed for SiO_2 and Al_2O_3. Evaluation of error in a *single* analysis, even without the SiO_2–Al_2O_3 complication, is a difficult matter and the present study offers no final solution.

APPENDIX

For those petrologists accustomed to the *C.I.P.W.* norms as a basis for evaluating chemical data, Table 8 will serve as the analogue of Table 6. Unlike the more comprehensive test, the norms here all have the same classification (Table 8, lower right). Individual values of doubtful significance are starred, as in Table 6. Quartz is definitely low relative to the standard norm; corundum is slightly higher. These trends are similar to those for SiO_2 and Al_2O_3 in Table 6. Orthoclase, albite, and enstatite are in satisfactory agreement with the standard norm; anorthite is notably higher than the standard.

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* These two standards are available in small quantities to responsible persons working in silicate chemistry. Inquiries should be directed to Dr. Michael Fleischer, Geological Survey, Department of the Interior, Washington, D. C.

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REFERENCE CITED

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BLOWPIPE PETROGRAPHY*

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ABSTRACT

An attempt is made to elicit interest in the use of the blowpipe as an auxiliary tool in the petrographic identification of non-metallic minerals. The customary flame colorations, bead tests, and fusibility determinations become subordinate to the new role of the blowpipe: the production of characteristic microscopic textures and products. The procedure involved in this simple and inexpensive method is outlined. The various thermal effects which may be utilized are briefly discussed. Several examples illustrating the application of the technique in the distinction of easily-confused minerals are presented.

INTRODUCTION

The accurate identification of non-metallic minerals under the polarizing microscope is often attended with difficulties. Not infrequently, positive identification is impossible without resorting to one or more confirmatory tests involving features other than their recorded optical properties. The microscopic characteristics of minerals treated at temperatures sufficiently elevated to induce decomposition, inversion, etc., furnish potential criteria for their identification. Indeed, the ceramic petrographer must often rely solely upon such characteristics in his optical study of finished ceramic products. Rather by necessity than by choice, he attempts to interpret the secondary textures and reaction products developed during calcination, in order to arrive at the identity of the original mineral constituents. The mineralogist-petrographer may well profit from the experience of his ceramic colleague by supplementing recorded optical properties with data furnished by the heat-treated minerals. He will find that the petrographic examination of a mineral both before and after calcination is often more fruitful than study of the uncalcined mineral alone.

The study of the effect of heat treatment on the non-metallic minerals has by no means been neglected by mineralogists, particularly those with an interest in the industrial use of these minerals. Abundant data, including dehydration curves, differential thermal curves, and heat-induced changes in optical properties, are scattered through the mineralogical literature. The growing popularity of differential thermal methods in the qualitative and quantitative analysis of non-metallic mineral mixtures is well known. To the writer's knowledge, however, little diagnostic use has hitherto been made of the changes occasioned in the optical properties of such minerals by heat treatment. Yet many non-metallic minerals, when thermally treated (as for example in the blowpipe flame), will be found to yield microscopically recognizable textures and products. This technique, which for convenience is termed "blowpipe petrography," is believed to merit greater attention in general petrographic practice. It is the purpose of this paper to outline the simple procedure involved, to discuss some typical effects which will be found useful, and to present a number of examples of their application.

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* Contribution from the Research Laboratories of the Ceramic Division of the Champion Spark Plug Company.

PROCEDURE

The technique herein referred to as "blowpipe petrography" is extremely simple. The only requirement in addition to the usual needs for petrographic study is a suitable means of heat-treating the specimens. A wide choice of methods is available for effecting calcination, choice being largely determined by the relative refractoriness of the material. A laboratory Bunsen burner has been found useful in some instances. The mineralogical blowpipe, which has all but disappeared from the modern mineralogical laboratory, is very satisfactory for many minerals. Much more convenient and versatile, however, is some such type as the National 3-A blowpipe,* equipped with tips for use with either gas and air, or gas and oxygen. Various other facilities may be utilized, such as laboratory furnaces, or production furnaces and kilns. These often permit fairly close control of temperature in a selected temperature range and over a prolonged period. The device described by Milton and Spicer (4), although never tested by the writer, would appear to offer a promising method for the rapid heat-treatment of small samples at a particular temperature.

As ordinarily practiced in the writer's laboratory, a very small sliver of the mineral being tested is held in the blowpipe flame by means of platinum-tipped forceps, much in the manner employed in standard blowpipe technique. In those cases in which the mineral is in the form of detrital grains or a fine-grained powder, the sample is wrapped in a small piece of platinum foil. For convenience the blowpipe is permanently mounted by clamps on a chemical burette-stand. In some instances in which fusion has occurred, it is desirable to quench the sample in water in order to preserve the glassy condition. In most cases, however, the sample is merely air-cooled by removal from the blowpipe flame. It is advisable to wear a pair of dark goggles during the blowpipe treatment. After calcination the mineral is powdered and examined according to regular powder-immersion procedure.

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* Manufactured by National Welding Equipment Company, San Francisco, California.

Some Typical Thermal Effects

A variety of thermal effects is encountered in the application of the blowpipe petrography technique. One such effect is complete fusion to a glass. This is akin to the well-known blowpipe fusibility test. But, whereas the latter test concerns itself merely with the relative tendency to fuse, blowpipe petrography involves the measurement of the refractive index of the glass, or the observation of the optical characteristics of the minerals which crystallize from the molten sample upon cooling. Another effect is that of incongruent melting in which the mineral partially melts with the liberation of another compound. A special case is that of liquid immiscibility, in which two liquid phases are formed. The phenomenon of polymorphic inversion is also very useful, in those instances in which re-inversion to the original form does not take place upon cooling. Some minerals which show little if any detectible cleavage can be induced to cleave by a sort of thermal shock treatment, thereby providing a lineation against which elongation and extinction can be measured. There are countless examples of hydrated minerals which may be reduced to the anhydrous oxides or silicates. Numerous carbonates may similarly be deprived of their volatiles to yield identifiable oxides. In the course of such dehydration or decarbonation, oriented or unoriented decomposition intergrowths are formed, which may prove to be quite diagnostic. The thermal behavior of some minerals may involve more than one of the above effects, as for example dehydration followed by polymorphic inversion. It is to be recommended, of course, that observations on relative fusibility, flame coloration, decrepitation, exfoliation, and other effects usually associated with standard use of the blowpipe, should also be made.

Some Typical Applications

One promising application of blowpipe petrography is the routine determination of the plagioclase feldspars. The refractive index of the fused feldspar is merely checked against a curve plotted from the data of Larsen (3). This method, which is theoretically capable of twice the accuracy obtainable from the measurement of the indices of the crystalline feldspars, is briefly described elsewhere (1).

The striking similarity of bastnäsite and xenotime in optical properties and in mode of occurrence has recently been emphasized (2). The most convenient method for differentiating the two minerals is brief calcination in the Bunsen burner flame, followed by microscopic examination of the calcine.

A commercial product labelled "calcium aluminate" was found to be optically isotropic, with refractive index of about 1.60. It would be natural to assume that this was the isotropic form of $5CaO \cdot 3Al_2O_3$. However, calcination in the burner flame resulted in the evolution of water. It was, therefore, concluded that the material was $3CaO \cdot Al_2O_3 \cdot 6H_2O$. This was confirmed by a careful ignition test, which yielded almost exactly the weight loss to be expected.

An unlabelled mineral sample gave optical data suggestive of topaz. This identification appeared reasonable, as topaz samples were known to be at hand. Blowpipe calcination, rather than indicating a refractory mineral, resulted in ready fusion and a characteristic lithia flame. Accordingly, it was tentatively identified as amblygonite. Further check revealed that a sample of amblygonite had recently been received for test as a ceramic flux.

A sample of kyanite from Colorado had associated with it a brownish needle-like mineral, the optical properties of which suggested either anthophyllite or sillimanite. Both minerals are known to occur with kyanite, with sillimanite the more probable associate. Blowpipe calcination caused complete breakdown of the acicular structure, and the liberation of dark opaque magnetic grains. Such behavior is to be expected of anthophyllite but not of sillimanite.

A specimen of Arizona corundum "ore" showed areas of a gray vitreous mineral which, because of the closely packed sillimanite needles, strongly suggested cordierite. Optical properties were difficult to obtain, due to the inclusions, but the indices pointed to either orthoclase or cordierite. Sillimanite inclusions are cited by Winchell (5) as a criterion for distinguishing cordierite from feldspar. However, blowpipe treatment fused the matrix of the sillimanite needles to a viscous glass of about 1.49 index, thus indicating that the matrix must be feldspar rather than cordierite.

A white fibrous mineral submitted by a prospector in the belief that it was sillimanite yielded optical properties coinciding with either an iron-free anthophyllite or xonotlite. Because of some attached serpentinous material and the comparative rarity of xonotlite, the mineral was tentatively identified as anthophyllite. However, a blowpipe test led to the production of pseudowollastonite, indicating that the original mineral was xonotlite.

A pitchy, black mineral from Ontario was labelled allanite, but correlation with allanite on the basis of optical properties was uncertain. The birefringence and indices were much lower than one would expect for a cerian epidote, and it was not possible to establish the optical character. Heating to a dull red heat strengthened the pleochroism, notably increased the indices and birefringence, and permitted determination of the biaxial negative character and large optic axial angle.

Among the fibrous and acicular minerals frequently forwarded to the Champion laboratories by prospectors in the belief that they are sillimanite, are wollastonite and tremolite. An excellent confirmatory test for wollastonite is the development of the mosaic texture of pseudowollastonite upon blowpipe calcination. Tremolite, too, gives a diagnostic texture upon such treatment. This texture consists of parallel needles of what is apparently a clinoenstatite-diopside solid solution with interstitial siliceous material, the needles showing inclined extinction up to about 32°.

Certain minerals which in crushed fragments display irregular grains, with no clue, in the form of visible cleavage traces, of crystallographic directions, can be induced to reveal lineation features upon ordinary blowpipe treatment. Thus, beryl grains develop almost parallel lines of bubbles, against which extinction is parallel and elongation positive. Andalusite, too, develops roughly parallel cracks, or zones of incipient mullitization, against which extinction is parallel and elongation negative. Cordierite likewise develops numerous close-set continuous or discontinuous cleavage traces against which extinction is parallel and elongation negative. More intense heat-treatment of andalusite and cordierite cause their decomposition to mullite and siliceous glass.

A soft, white massive sample exhibited indices of refraction between 1.52 and 1.53. These properties suggested gypsum, but because of the microcrystalline nature of the mosaic aggregate texture, additional optical properties were unobtainable. Blowpipe calcination yielded large equidimensional grains of high birefringence and indices between 1.57 and 1.61. Since these latter characteristics agree with anhydrite, the blowpipe test may be considered as confirmation of the tentative identification of the original material as gypsum.

The above enumeration includes by no means all of the instances in which the blowpipe petrography technique has been successfully applied. Other cases which might be briefly cited are: the distinction of sillimanite and mullite by reason of the tendency of sillimanite to form mullite above 1600° C.; the differentiation of monticellite and forsterite by virtue of the formation of periclase by the former; the confirmation of sapphirine by its development of spinel crystals; verification of gamma dicalcium silicate, of tricalcium silicate and certain of the hydrated calcium silicate minerals through their conversion to larnite; identification of diaspore, beta-alumina and alunite through their formation of corundum; the unmistakable criterion of andalusite in its well-known parallel mullite-cristobalite aggregates; the distinction between pyrope and spinel by means of the decomposition of the garnet as contrasted with the stability of spinel; the formation of periclase as a clue to the identity of brucite, hydromagnesite, magnesite, and dolomite; the complete decomposition of jadeite to yield albite and nepheline between 800° and 1000° C.; the decomposition of phenacite into its constituent oxides above 1600° C.; the characteristic melting of danburite to form two immiscible liquids; the restoration of the normal optical properties of a number of metamict minerals.

CONCLUSION

It has been the purpose of this paper to try to interest the student and the practicing petrographer in the potentialities of the blowpipe petrography technique. To that end, it did not appear needful to present an exhaustive list of all of its possible applications. Nevertheless, the writer is currently compiling the widely scattered data on the thermal behavior of the non-metallic minerals, with the view to their more convenient use as diagnostic criteria. Although no systematic scheme has been devised, as in the case of standard optical properties, such is neither necessary nor, perhaps, desirable. At best, the blowpipe petrography technique is to be looked upon as a confirmatory step, subordinate and supplementary to the standard petrographic procedure. That it has distinct possibilities in this direction should be apparent from the selected examples discussed above.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to the officials of the Champion Spark Plug Company, particularly to F. H. Riddle and H. F. Royal, for permission to publish this paper.

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REGULARITIES IN THE INFRARED ABSORPTION SPECTRA OF SILICATE MINERALS

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ABSTRACT

In order to augment the published infrared data on silicate minerals so that any relationship between spectra and structures might be revealed, the infrared absorption spectra of eighteen silicates have been measured from 2 to 15 microns. These spectra were obtained from thin films of powder having particle diameters less than 2 microns. Study of all available silicate spectra shows that the infrared spectrum can be used to characterize the type of silicon-oxygen group. The groups that have been considered are the isolated SiO_4 tetrahedron, Si_3O_9 ring, single chain, double chain, layer, framework, and silica. The region of strongest absorption tends to shift toward shorter wave length as the ratio of silicon to oxygen increases.

INTRODUCTION

Although the absorption of infrared radiation by minerals was first studied a half century ago (1, 2), it was not until recent years that the commercial availability of accurate, automatic-recording infrared spectrometers enabled mineralogists to take advantage of the possibilities afforded by this exceedingly useful tool. The present work concerns the contributions of infrared spectroscopy to the knowledge of the structures of silicate minerals.

The atoms of a solid are constantly vibrating about their equilibrium positions with frequencies of 10^{12} to 10^{14} cycles per second. Because infrared or heat rays have frequencies in this range, it is possible to determine some of these vibration frequencies by either of two methods. In the absorption method, infrared radiation is passed through a solid; if the frequency of the radiation coincides exactly with a vibration frequency, the solid absorbs some or all of the infrared radiation of this frequency. The reflection method is based on the principle that the reflecting power of a solid increases rapidly in the vicinity of a strong vibration frequency; the reflection maxima show the approximate positions of strong vibration frequencies.

The selective absorption of infrared radiation by silicate minerals has been known since the early 1900's, when Coblentz (1, 2) obtained infrared absorption spectra of cleavage sheets or polished sections of many silicates. The slices he used were about 0.1 mm. thick; they were opaque to infrared radiation having wave lengths longer than 9 microns. Coblentz also examined the reflecting power of polished surfaces of minerals and found that the silicates had reflection maxima in the region of 9 to 12 microns. He made the important observation that "the various silicates have quite different reflection spectra."

In the 1930's Schaefer *et al.* (3) and Matossi and Krüger (4) published the infrared reflection spectra of some silicate minerals. Matossi and Bronder (5) examined the infrared absorption, in the range 2 to 8 microns, of plates cut from silicate crystals. They assigned the absorption bands observed in this region to combination and overtone frequencies derived from the longer-wave length fundamental vibrations, whose approximate positions were known from reflection spectra. As in the pioneering work of Coblentz, the samples they examined were opaque to wave lengths longer than 9 microns, and the positions of the strong fundamental-vibration frequencies in this region could not be obtained by absorption measurements.

An outstanding advance in experimental technique resulted from the work of Pfund (6) and of Barnes *et al.* (7), who showed that the infrared absorption spectrum of a solid could be obtained by using a thin film of powder, provided that the powder particles had diameters smaller than the wave length of the infrared radiation. When the particle size was larger than the wave length, the infrared rays were refracted and emerged from the layer in random directions giving an apparent opacity; when the particles were smaller than the wave length, they did not act as refracting centers. The greatest exponent of the powder technique has been Lecomte (8), who used it to obtain the infrared spectra of many inorganic compounds containing polyatomic anions such as PO_4, SO_4, and HCO_3.

The powder technique has only recently been applied to the study of the silicates. Keller and Pickett obtained infrared spectra of some clays (9) and silica minerals (10). A report by Adler *et al.* (11), under the aegis of the American Petroleum Institute, consists of a collection of infrared studies of clay minerals made at several laboratories. In many of the published powder-film spectra the absorption bands are poorly defined because of large-particle scattering. Hunt *et al.* (12), who obtained spectra of several silicates, used only particles having diameters less than 5 microns, with the result that their silicate spectra show well-defined absorption bands.

In principle, it is possible to calculate theoretically the vibration frequencies for a solid; however, except for very simple structures, formidable mathematical difficulties are encountered. In such instances it is convenient to adopt an empirical approach that has been useful in the determination of the structures of organic compounds. This approach consists of comparing the infrared spectra of a series of compounds, each containing the same group of atoms. Often such comparisons show that certain groups of atoms have characteristic vibration frequencies giving rise to absorption bands which persist in different compounds.

Table 1. Minerals Used in This Study

Mineral	Formula	Locality	Source	Remarks
Forsterite	Mg_2SiO_4	Italy	Ward's Natural Science Establishment, Inc., Rochester, New York	
———	β-Ca_2SiO_4	(Synthetic)	Prepared by K. R. Bonnickson, Pacific Experiment Station, Bureau of Mines	Preparation and properties described in reference (13).
Willemite	Zn_2SiO_4	Franklin, Sussex County, New Jersey	Author's collection	Green. Fluoresces strongly under ultraviolet light.
Phenacite	Be_2SiO_4	San Miguel di Piracicaba, Minas Geraes, Brazil	Chicago Natural History Museum	Colorless lenticular crystals.
Zircon	$ZrSiO_4$	Henderson County, North Carolina	Ward's	Crystals, ca. 1 cm. long.
Kyanite	Al_2OSiO_4	Clarkesville, Georgia	Ward's	Bladed crystals.
Benitoite	$BaTiSi_3O_9$	San Benito County, California	Smithsonian Institution, United States National Museum	Fragments of semi-transparent blue crystals. Smithsonian catalog no. 86539.
Rhodonite	$MnSiO_3$	Plainfield, Massachusetts	Ward's	Pink, massive. Infrared spectrum shows a carbonate impurity.
Enstatite	$(Mg,Fe)SiO_3$	Chester County, Pennsylvania	Chicago Natural History Museum	Bronzite variety.
Enstatite	$(Mg,Fe)SiO_3$	North Carolina	Ceramic Division, Champion Spark Plug Company	Bronzite variety. Reference (14).
Clinoenstatite	$MgSiO_3$	(Synthetic)	Ceramic Division, Champion Spark Plug Company	Reference (14).

TABLE 1 (*Continued*)

Mineral	Formula	Locality	Source	Remarks
Aegirite	$NaFe(SiO_3)_2$	Langesundfjord, Norway	Chicago Natural History Museum	Black, prismatic, vertically striated crystals. *X*-ray diffraction pattern agrees with values in *A.S.T.M.* index.
Jadeite	$NaAl(SiO_3)_2$	Tibet	Chicago Natural History Museum	Green. *X*-ray diffraction pattern agrees with values in *A.S.T.M.* index.
Spodumene	$LiAl(SiO_3)_2$	near Keystone, South Dakota	Ward's	White, cleavable.
Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	Bakersville, Mitchell County, North Carolina	Ward's	Asbestos-like variety.
Hornblende	$(Ca,Na,K)_{2-3}(Mg,Fe,Al)_5(Si,Al)_2Si_6O_{22}(OH)_2$	Arendal, Norway	Chicago Natural History Museum	*X*-ray diffraction pattern agrees with values in *A.S.T.M.* index.
Attapulgite	$Mg_5Si_8O_{20}(OH)_2 \cdot 8H_2O$	Gadsden County, Florida	American Petroleum Institute Project No. 49	Collected and identified by American Petroleum Institute Project No. 49, Clay Mineral Standards. Sample no. H-43.
Sepiolite	$(Mg,H_2)_3Si_4O_{11} \cdot H_2O \cdot (H_2O)_x$	near Pinos Altos, New Mexico	Ward's	White, amorphous. *X*-ray diffraction pattern shows lines due to sepiolite, calcite, and α-quartz.
Orthoclase	$KAlSi_3O_8$	Fort Bayard, New Mexico	Ward's	Large white crystals.

The purposes of the present work are to present the infrared absorption spectra of eighteen silicate minerals, to compare these spectra with those which have appeared in the literature, and to point out certain similarities in the spectra of minerals having the same type of silicon-oxygen group.

EXPERIMENTAL

The minerals used in this study are described in Table 1. They were selected because their absorption spectra were needed to complement published infrared data on silicates.

The infrared absorption spectra were obtained using thin films of powder having particle diameters less than 2 microns. To isolate particles of this size, about 2 g. of the silicate, ground to pass a 300-mesh screen, was shaken with 100 ml. of C.P. isopropyl alcohol in a glass-stoppered, 100-ml. graduated cylinder. The suspension was then allowed to stand 16 hours or longer. At the end of this time an upper layer of the suspension was drawn off to include only particles finer than 2 microns, the depth of this layer being calculated from Stokes' law. A serviceable form (15) of Stokes' law for this calculation is:

$$S=\frac{D^2g(\rho_1-\rho_2)(T\times 60)}{18\eta\times 10^8}$$

where S = distance in cm. fallen by particle in T minutes,
D = diameter of particle in microns,
g = acceleration of gravity (980 cm./sec.^{2}),
ρ_1 = density of the particle (g./ml.),
ρ_2 = density of the liquid (g./ml.),
η = absolute viscosity of the liquid (poises).

Isopropyl alcohol rather than water was chosen as a sedimenting liquid because of the work of Webb (15), who showed that during the sedimentation of silica-alumina cracking catalysts flocculation occurs in water but not in isopropyl alcohol.

The isopropyl alcohol suspension withdrawn was evaporated to 15 ml. and centrifuged. Most of the supernatant alcohol was drawn off, the powder and remaining alcohol were stirred, and a few drops of the resulting slurry were transferred with a 1-ml. hypodermic syringe to a weighed sodium chloride plate. When the alcohol evaporated, a thin film of powder was left on the plate, which was again weighed. The weight of the film divided by the area of the plate was recorded on the spectrum in mg./cm.^{2}

The spectra were obtained on a Beckman *IR*2 infrared spectrometer equipped with a sodium chloride prism. The wave-length scale was calibrated against known absorption maxima of liquid toluene and of atmospheric water vapor and carbon dioxide. The slits were automatically adjusted by means of a slit drive. The I_0, or reference, curve was obtained by recording the radiant power transmitted by a sodium chloride plate having the same dimensions as the plate used to support the sample. The I, or sample, curve was obtained by recording the radiant power transmitted by the powder-coated plate.* The repeatability of a recorded curve obtained using the slit drive was about ±0.3% of the recorder chart width. Wave lengths were accurate to ±0.02 micron. A typical recording is shown in Fig. 1. Percent-transmission curves were obtained from these recordings by measuring the ratio I/I_0 in a point-by-point manner. Measurements of percent transmission ($I/I_0 \times 100$) were then transcribed to a chart having a linear wave-length scale.

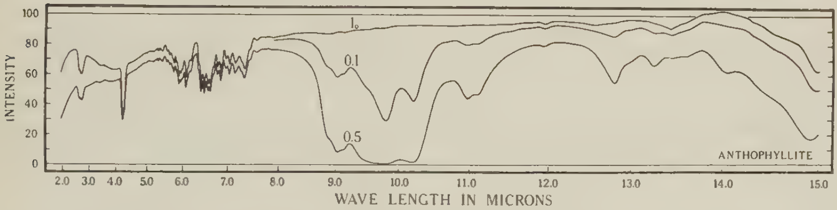

FIG. 1. Automatically recorded infrared curves of anthophyllite. I_0 curve shows radiant power transmitted by a sodium chloride plate. Values on lower curves give sample thicknesses in mg./cm.².

The spectra of the eighteen minerals studied are shown in Figs. 2–5, and the positions of the absorption bands are listed in Table 2. Each spectrum has a transmission maximum at or near 8 microns and transmission minima, or absorption bands, in the range of 8 to 15 microns. Scattering by refraction is responsible for the percent-transmission decrease at the lower end of the wave-length scale. Many of the spectra show a weak band at 6.1 microns due to a small amount of entrained water. The 6.1-micron bands are stronger in the spectra of attapulgite and sepiolite, two silicates which contain water of crystallization. The early researches of Coblentz (1) showed that both water of crystallization and liquid water absorb strongly at 6.1 microns.

* In order to obtain reproducible intensities, it is important to compare the I_0 and the I sodium chloride plates for equal infrared transmission before each sample preparation. Plates with non-parallel faces cause a prismatic deviation of the infrared beam with a subsequent decrease in the amount of energy reaching the thermocouple. The natural cleavage planes of sodium chloride, lightly polished with jeweler's rouge, make good parallel surfaces.

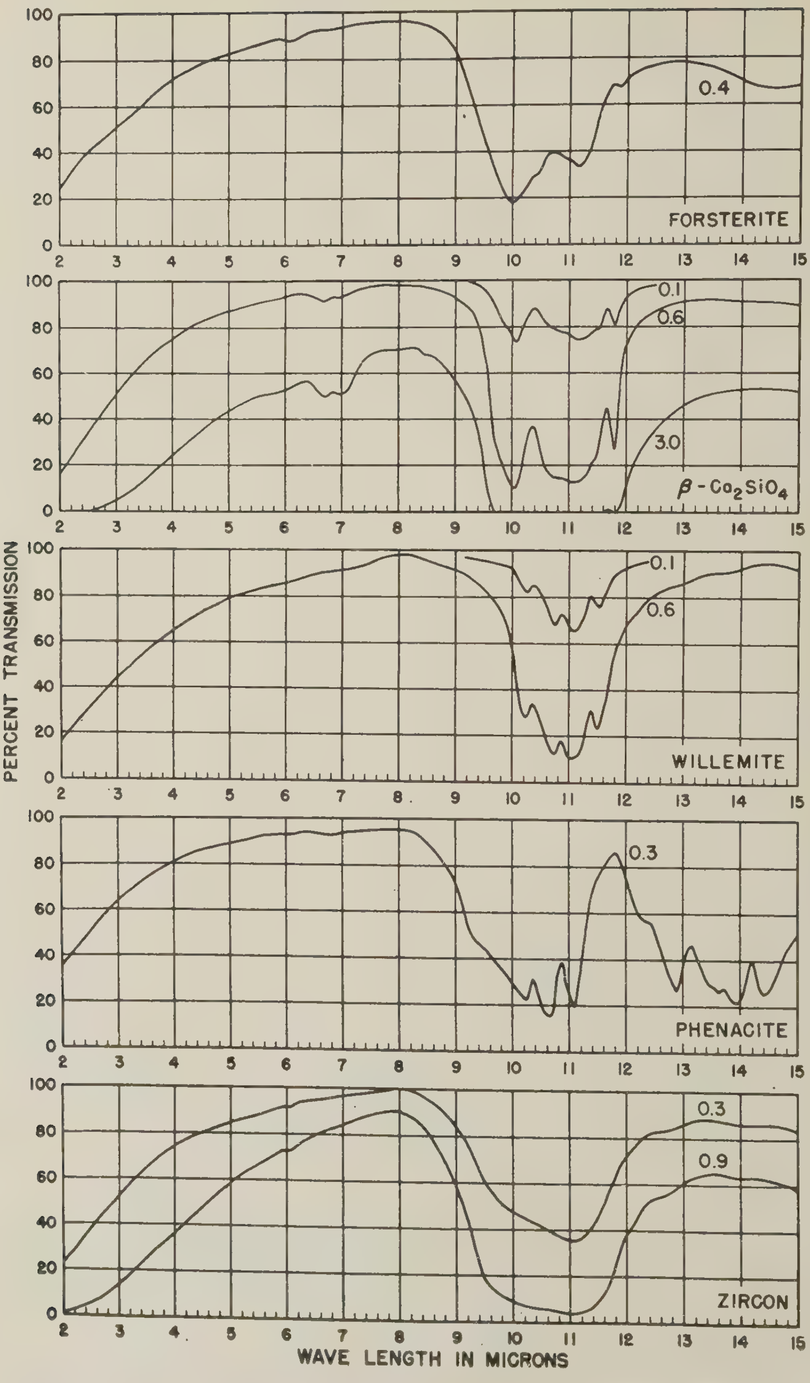

Fig. 2. Infrared absorption spectra of forsterite, β-Ca_2SiO_4, willemite, phenacite, and zircon.

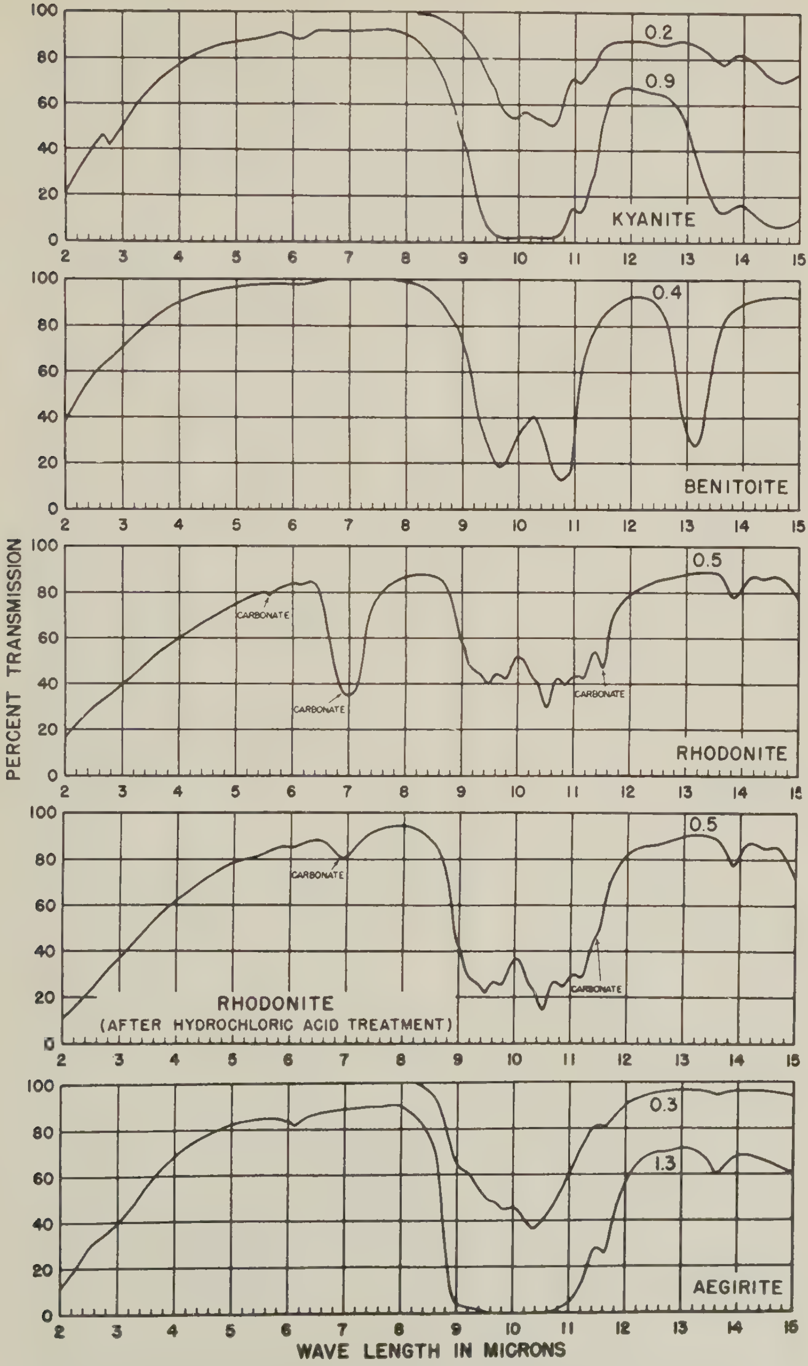

FIG. 3. Infrared absorption spectra of kyanite, benitoite, rhodonite, and aegirite.

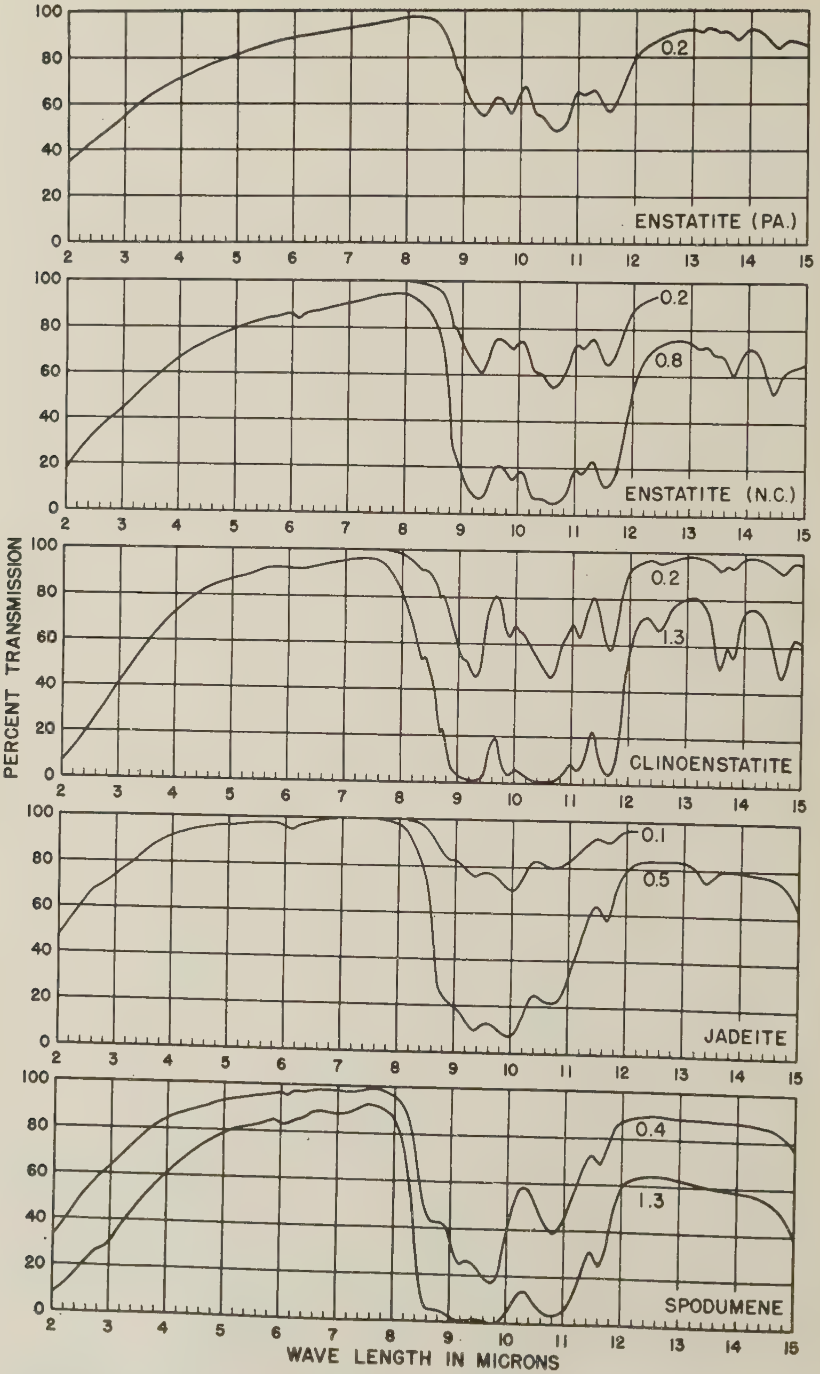

FIG. 4. Infrared absorption spectra of enstatite, clinoenstatite, jadeite, and spodumene.

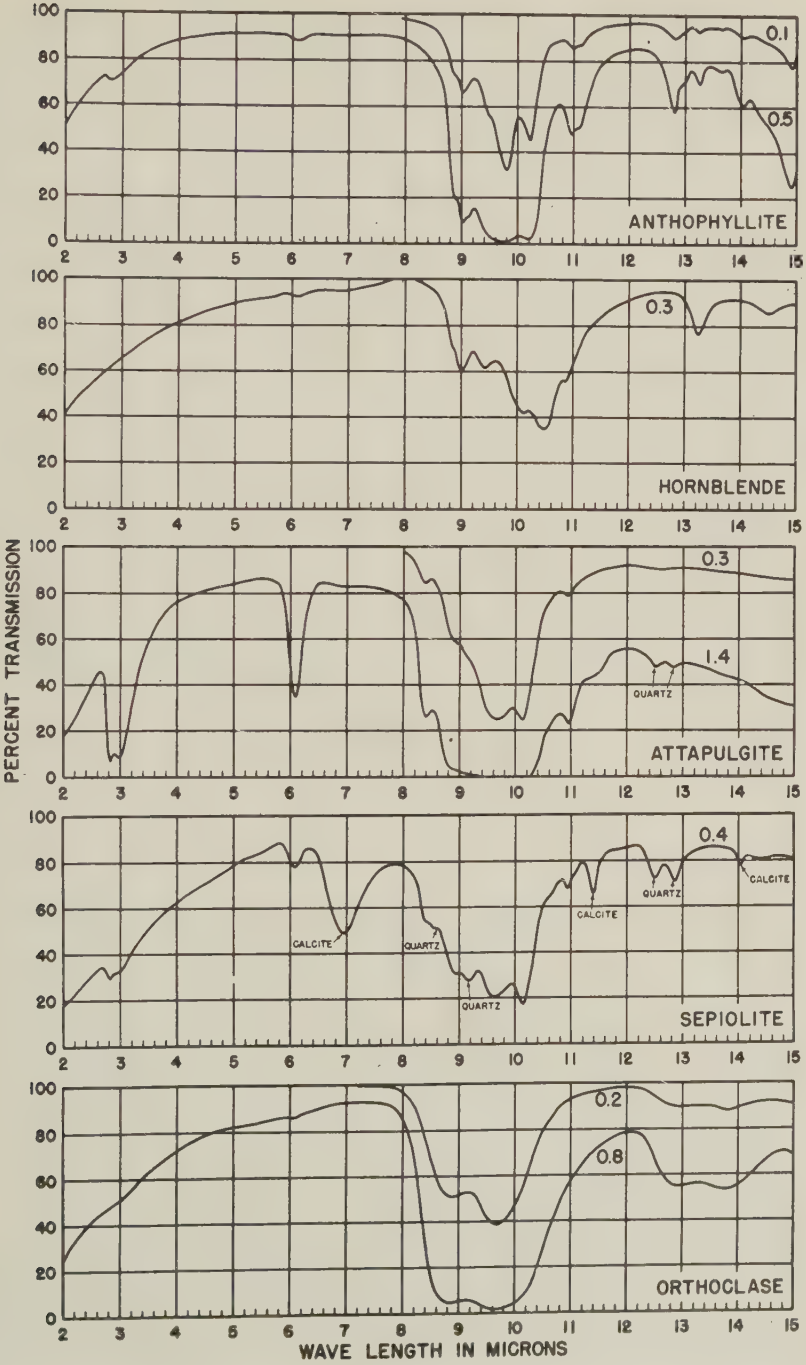

FIG. 5. Infrared absorption spectra of anthophyllite, hornblende, attapulgite, sepiolite, and orthoclase.

TABLE 2. POSITIONS OF INFRARED ABSORPTION BANDS

Mineral	Wave Length in Microns						
Forsterite			10.00 10.45	11.17 11.89			
β-Ca$_2$SiO$_4$		9.7	10.04 10.7	11.1 11.5 11.78			
Willemite			10.25 10.74	11.10 11.52			
Phenacite		9.3	10.25 10.66 10.95	11.10	12.3 12.90	13.45 13.62 13.94	14.40
Zircon		9.7		11.05			
Kyanite		9.5 9.92	10.3 10.58	11.10 11.35		13.62	14.65
Benitoite		9.66	10.75[a]			13.13	
Rhodonite	8.95	9.18 9.47 9.75	10.28 10.51 10.85	11.17		13.88	
Enstatite	8.86	9.35 9.90	10.28 10.62	11.09 11.55		13.18 13.42 13.75	14.44
Clinoenstatite	8.35 8.68	9.07 9.29 9.88	10.08 10.62	11.12 11.65	12.50	13.57 13.80	14.63
Aegirite		9.00 9.55 9.84	10.35	11.62		13.62	
Jadeite	8.85	9.35 9.97	10.70	11.65		13.40	
Spodumene	8.65	9.16 9.70	10.80	11.60			
Anthophyllite	8.86	9.02 9.11 9.46 9.79[b]	10.21 10.97	11.11	12.80	13.00 13.25 13.64	14.03 14.90
Hornblende	8.84	9.01 9.43	10.14 10.49 10.87			13.25	14.52
Attapulgite	8.39 8.87	9.68	10.12 10.95				
Sepiolite	8.38 8.92	9.64	10.13 10.93				
Orthoclase	8.85	9.66			12.90	13.75	

[a] Possibly has a shoulder at 10.87 microns.

[b] Band center uncertain, because talc, a possible contaminant, has its strongest band at 9.8 microns.

The spectrum of rhodonite, in Fig. 3, shows absorption bands due to a carbonate at 5.58, 7.0, and 11.51 microns. The positions of these bands strongly suggest that the carbonate is rhodochrosite, $MnCO_3$, reported to have absorption maxima at 5.58, 7.0, and 11.50 microns (12). As a confirmatory test for carbonate, an infrared spectrum was obtained of rhodonite which had been treated with hydrochloric acid. In the spectrum of acid-treated rhodonite the carbonate bands are weaker and the silicate bands are stronger.

Both the infrared spectrum, shown in Fig. 5, and an x-ray powder photograph reveal the presence of α-quartz and calcite in the sepiolite sample used for this study. Seven infrared bands can be accounted for by α-quartz (8.6, 9.2, 12.53, 12.83 microns) and calcite (6.95, 11.40, 14.03 microns).

An absorption spectrum of hornblende published by Hunt *et al.* (12) has bands at 9.8 and 14.95 microns and is unlike the spectrum shown in Fig. 5 for the hornblende sample used in the present study and authenticated by x-ray diffraction.

DISCUSSION OF RESULTS

The silicon-oxygen groups to be considered in this report are arranged according to the x-ray-determined structural classification of W. L. Bragg:

I. Isolated SiO_4 tetrahedron
II. Si_3O_9 ring
III. Single chain
IV. Double chain
V. Layer
VI. Framework
VII. Silica

In order to ascertain whether infrared absorption can be used to characterize the various types of silicon-oxygen groups which occur in minerals, the experimental results are summarized and correlated with published infrared data by means of the bar charts shown in Figs. 6–12. In these charts, strong infrared bands are depicted by tall bars and weak bands by short bars. Some published spectra were not included because the identity of the silicate was in doubt or because the bands were poorly defined. If the absorption spectrum of a silicate was not available but its reflection spectrum was known, the reflection spectrum (labelled R) was used in the bar charts. The reflection maxima serve to indicate the approximate wave lengths at which absorption bands are expected to occur. Since the reflection method gives only the strong vibration frequencies, the reflection spectrum will usually show less detail than the absorption spectrum.

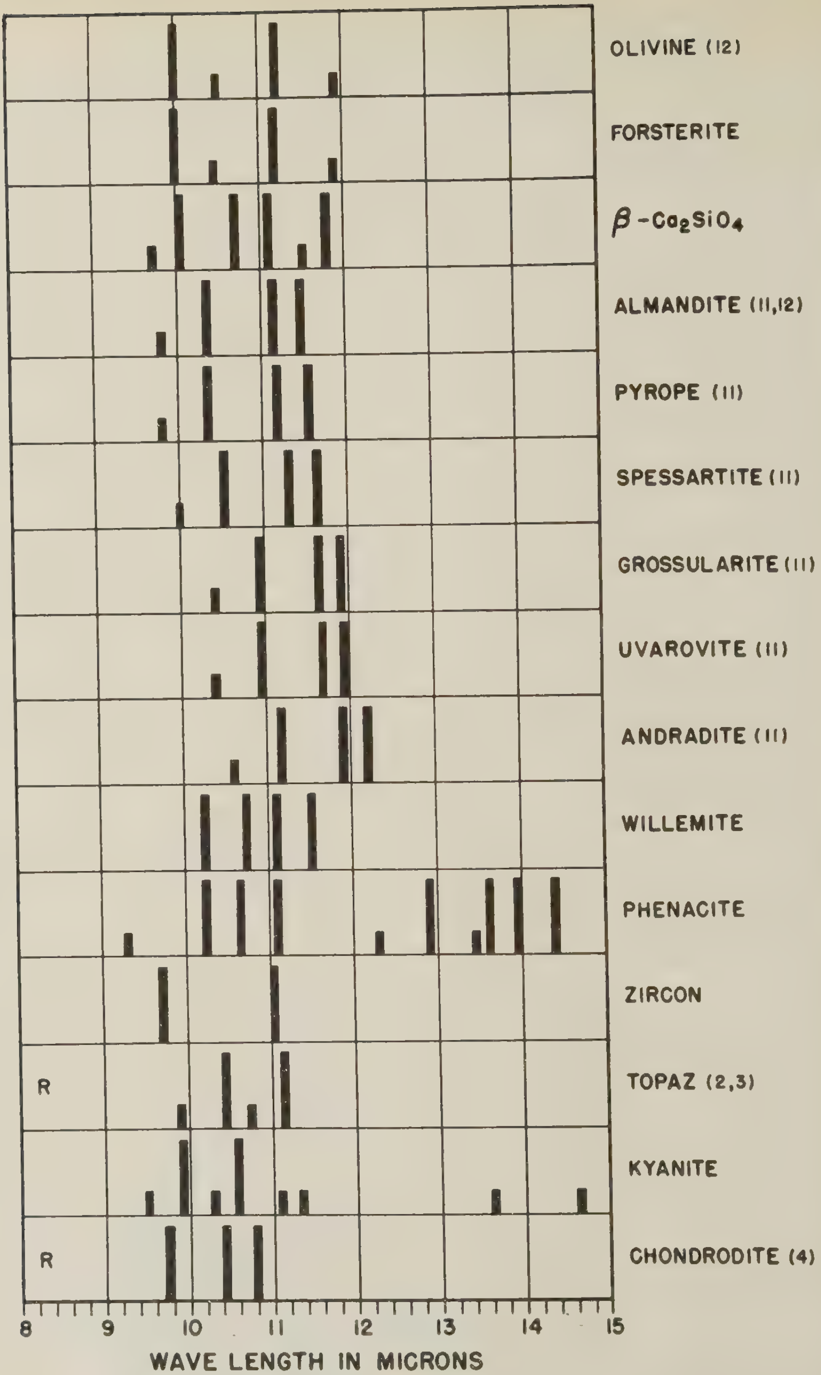

FIG. 6. Infrared absorption maxima of silicates containing the isolated SiO_4 tetrahedron.

"R" indicates the reflection spectrum. Spectra from the literature are identified by reference numbers.

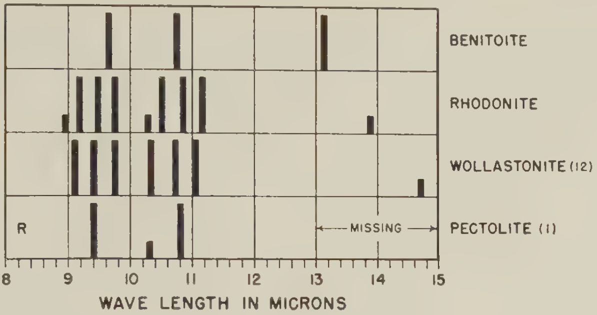

FIG. 7. Infrared absorption maxima of benitoite and other silicates that may contain the Si_3O_9 ring.

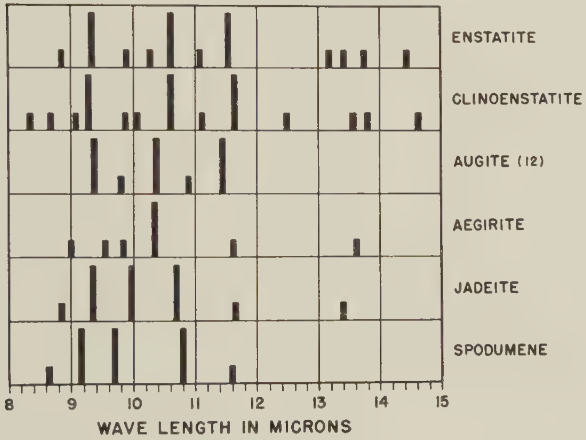

FIG. 8. Infrared absorption maxima of single-chain silicates.

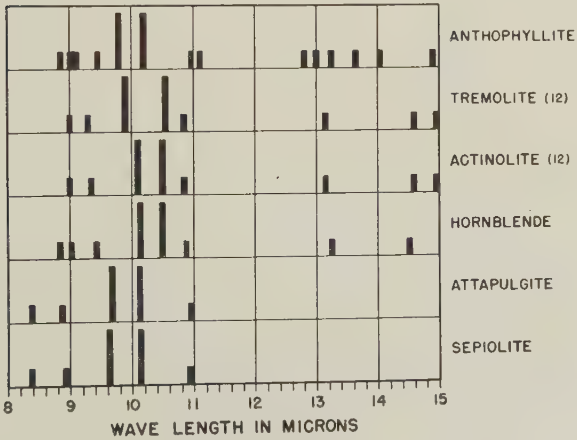

FIG. 9. Infrared absorption maxima of double-chain silicates.

Isolated SiO_4 Tetrahedron

Infrared data on orthosilicates are collected in Fig. 6. All of these orthosilicates have two, three, or four strong bands in the range of 10 to 12 microns. Since these compounds embrace a variety of positive ions and crystal structures, it is reasonable to assign these bands to vibrations of the independent SiO_4 group, which all orthosilicates have in common.

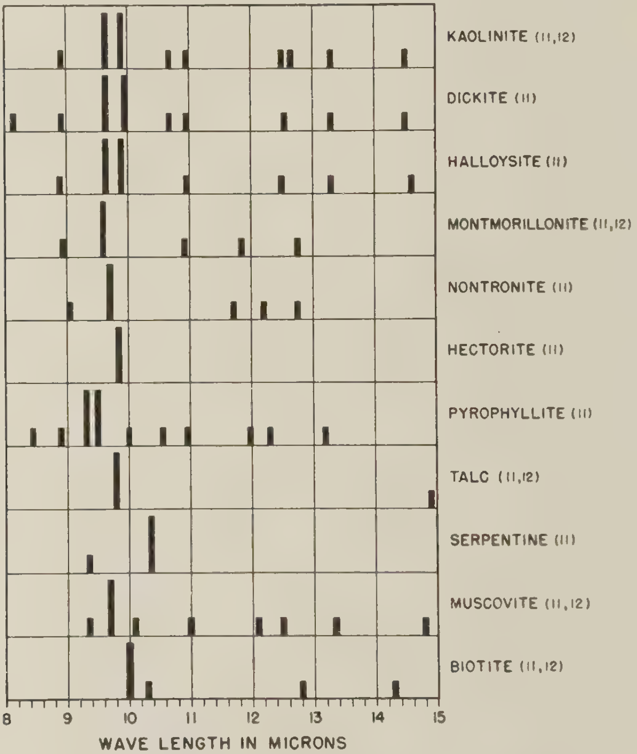

FIG. 10. Infrared absorption maxima of layer silicates.

The absorption spectra of olivine and forsterite are very nearly identical. Synthetic β-Ca_2SiO_4 has a spectrum similar to the spectra of olivine and forsterite. A weak band at 11.9 microns in the olivine and forsterite spectra corresponds to a sharp, much stronger band at 11.78 microns in the β-Ca_2SiO_4 spectrum.

The spectra of the garnet minerals (almandite to andradite) were obtained by Adler (11), who found that the absorption bands of the garnets shift to longer wave lengths as the lattice constant increases.

Phenacite, Be_2SiO_4, and willemite, Zn_2SiO_4, the two major silicates of the phenacite group, have strikingly similar absorption bands at 10.25, 10.7, and 11.1 microns, despite a sevenfold difference in the atomic weights of the cations. Phenacite has strong absorption bands between 12 and 15 microns—a region where most of the other orthosilicates do not absorb. It is reasonable to attribute these bands, and possibly the 9.3-micron band, to Be-O vibrations. By the same reasoning, the kyanite 13.6- and 14.6-micron bands are thought to be due to Al-O vibrations.

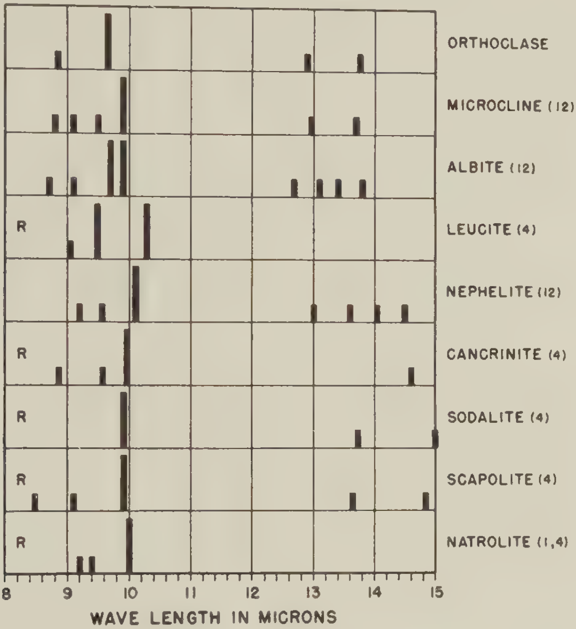

FIG. 11. Infrared absorption maxima of framework silicates.

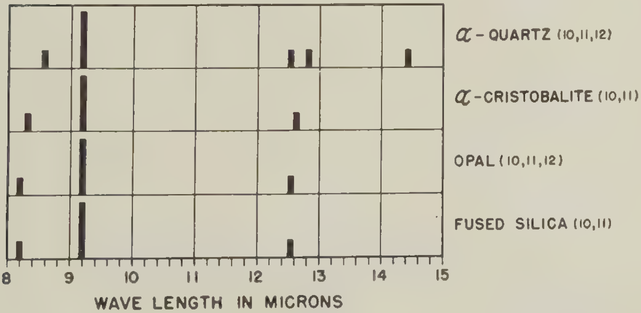

FIG. 12. Infrared absorption maxima of silica minerals.

The spectrum of zircon shows less structure than the spectra of the other orthosilicates. There is some arbitrariness in selecting 9.7 microns as the center of the shorter wave-length band.

The reflection maxima of topaz, $Al_2SiO_4F_2$, and chondrodite, $2\ Mg_2SiO_4 \cdot Mg(F,OH)_2$, fall in the region of the spectrum where the other orthosilicates have their characteristic absorption maxima.

Si_3O_9 Ring

Spectra of benitoite, rhodonite, wollastonite, and pectolite are compared in Fig. 7. Benitoite, in which the silicate ion is known to consist of three tetrahedra linked corner to corner in a ring to form Si_3O_9 (16), has strong bands at 9.66, 10.75, and 13.13 microns. The band at 13.13 microns occurs in a region where most silicates do not have strong absorption bands.

Structure determinations of rhodonite, $MnSiO_3$, and wollastonite, $CaSiO_3$, are not available; however, these silicates are thought to contain Si_3O_9 rings. Benitoite's single bands at 9.66 and 10.75 microns appear as triplets in rhodonite and wollastonite. If rhodonite and wollastonite have Si_3O_9 rings, it is surprising that they lack the strong band in the 13-micron region shown by benitoite. Although these data neither confirm nor disprove the presence of Si_3O_9 rings in rhodonite and wollastonite, the marked similarity of the spectra of these two minerals leaves no doubt that rhodonite and wollastonite contain the same type of silicate ion.

Pectolite, $NaHCa_2(SiO_3)_3$, which is reported (17) to be isomorphous with wollastonite and possibly to have an analogous structure, has strong reflection maxima at 9.4 and 10.8 microns. These maxima correspond to the centers of the wollastonite trifurcated absorption regions. To confirm the structural similarity of pectolite with wollastonite, an absorption spectrum of pectolite is needed.

Single Chain

Infrared spectra of six pyroxenes are compared in Fig. 8. With the exception of aegirite, all of these single-chain silicates have three strong bands between 9 and 12 microns.

The spectra of the $MgSiO_3$ polymorphs, enstatite and clinoenstatite, have the same over-all appearance but show small differences in the wave lengths of two of the strong absorption bands and numerous differences in the weak absorption bands.

Augite, $CaMg(SiO_3)_2$, has three strong absorption bands like those of enstatite and clinoenstatite, but its spectrum shows fewer weak bands.

The resemblance of the 11.6-micron bands of aegirite, jadeite, and spodumene suggests that in all three minerals these bands are due to the same kind of vibration. Jadeite, $NaAl(SiO_3)_2$, and spodumene, $LiAl(SiO_3)_2$, have very similar absorption spectra. In this pair, the substitution of Na^+ for Li^+ causes a bathochromic shift of four absorption bands.

Double Chain

The double-chain silicates, whose spectra are depicted in Fig. 9, have two strong absorption bands near 10 microns, two or more weak bands between 8.4 and 9.5 microns, and another weak band near 10.9 microns. The four amphiboles have a band near 13 microns.

Attapulgite, a clay with a double-chain structure (18), has a spectrum which lacks the 13-micron band of the amphiboles. The examination of a 1.4 mg./cm.^{2} layer (Fig. 5) confirmed the absence of a 13-micron band but did reveal bands at 12.53 and 12.83 microns characteristic of α-quartz, an impurity which was not detected from an x-ray powder photograph of this sample.

The five absorption bands of sepiolite coincide in positions (within a few hundredths of a micron) and relative intensities with the bands of attapulgite. The infrared spectrum of sepiolite supports the double-chain silicate structure proposed for sepiolite by Longchambon (19).

Layer

Absorption data on minerals containing silicon-oxygen sheets are collected in Fig. 10. Despite the complexity of these minerals, they all have one or two strong absorption bands between 9.4 and 10.4 microns. It is reasonable to assign this strong absorption to a vibration characteristic of a silicon-oxygen layer, the only grouping of atoms which all of these minerals have in common.

Another interesting regularity is that the substitution of magnesium for aluminum reduces the number of absorption bands and causes the strong silicon-oxygen band to undergo a bathochromic shift. These effects are illustrated by going from pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, to talc, $Mg_3Si_4O_{10}(OH)_2$; and from muscovite, $KAl_2AlSi_3O_{10}(OH)_2$, to biotite, $KMg_3AlSi_3O_{10}(OH)_2$. In the series (20) of related clays: montmorillonite, nontronite, and hectorite, these effects are apparent in going from the spectra of montmorillonite and nontronite to the spectrum of hectorite, the aluminum-free magnesium end-member of the series.

Serpentine, originally described as a double-chain structure, has been classed by Warren (21) with the layer structures. The dissimilarity of the spectrum of serpentine and the spectra of the double-chain silicates supports this change.

Framework

A comparison of infrared data on framework structures, given in Fig. 11, shows that the silicon-oxygen framework, like the layer, tends to absorb strongly near 10 microns. All of the absorption spectra and some of the reflection spectra show weak bands in the region of 13 to 15 microns.

The difference between the infrared absorption spectra of two crystal forms of $KAlSi_3O_8$, orthoclase and microcline, shows again that the infrared spectrum of a mineral depends not only upon chemical constitution but also upon the way in which the atoms are arranged in the crystal structure.

Nephelite, once classed with the orthosilicates, now is known to have a tridymite-like framework (17). The similarity of the nephelite spectrum to the spectra in Fig. 11, along with the absence in nephelite of a second strong band near 11 microns (cf. Fig. 6), is consistent with a framework structure.

Silica

Infrared absorption maxima of α-quartz, α-cristobalite, opal, and fused silica are shown in Fig. 12. These silica minerals have in common a

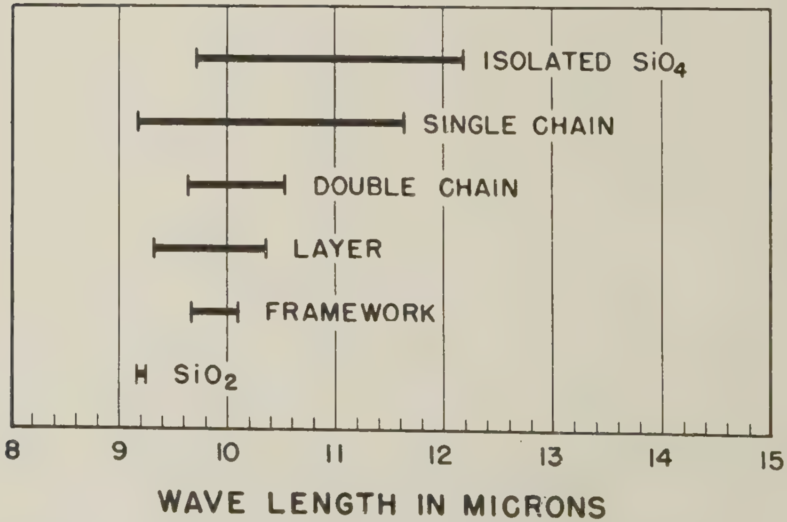

Fig. 13. Wave-length ranges of strong infrared absorption bands of silicon-oxygen groups.

strong 9.2-micron absorption band and weaker bands between 8.2 and 8.6 microns and between 12.5 and 12.8 microns.

CONCLUSION

A chart showing the wave-length ranges of the strong infrared absorption bands of silicon-oxygen groups is given in Fig. 13, where the region in which strong bands occur is shown by a horizontal line to the left of each group. The silicon-oxygen groups here are arranged according to an increasing ratio of silicon to oxygen. As the Si:O ratio progresses from 0.25 in the isolated SiO_4 tetrahedron to 0.50 in silica, the region of strong absorption shifts to shorter wave lengths, and the wave-length ranges tend to narrow.

One of the best features of the infrared spectrum is that absorption or lack of absorption at certain wave lengths often can be correlated with the type of silicon-oxygen group in the mineral. Small displacements of the vibration frequencies characteristic of a silicon-oxygen group must arise mainly from the fact that these vibrations are not completely independent of the rest of the crystal. It is to be hoped that such frequency shifts ultimately can be interpreted to give information about the structure adjacent to the silicon-oxygen group.

ACKNOWLEDGMENTS

The author is indebted to L. J. Schmauch of this Laboratory for the design and construction of the automatic slit drive for the infrared spectrometer; and to W. A. Kimball, also of this Laboratory, for carrying out the *x*-ray diffraction studies. He wishes to thank the following persons for generously supplying specimens: Robert K. Wyant, Chicago Natural History Museum; Wilfrid R. Foster, Champion Spark Plug Company; K. K. Kelley, Pacific Experiment Station, Bureau of Mines; George Switzer and C. Lewis Gazin, United States National Museum.

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PROBABLE IDENTITY OF BELYANKITE WITH CREEDITE*

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Abstract

Optical and *x*-ray data, crystal form, and differential thermal analyses suggest that belyankite (Dorfman, 1950) is creedite and that the analysis of belyankite is incorrect.

In reading the description of an apparently new calcium aluminum fluoride recently described and named belyankite by Dorfman (Dorfman, 1950), it was noticed that the formula, $Ca_2Al_3(F,OH)_{13} \cdot H_2O$, calculated by him was in error, the analysis as given actually yielding the simpler formula $Ca_3Al_2F_{12} \cdot 4H_2O$. In other respects, however, the description of belyankite, which also included optical, *x*-ray, and differential thermal analysis data, seemed at first sight to be a satisfactory account of a new species.

Dr. W. T. Schaller, in discussing the error of calculation with me, pointed out the great similarity of the crystal drawing of belyankite to those of creedite and suggested that the supposedly new mineral might indeed be creedite.

Table 1. Comparison of Analysis of Belyankite with Analyses of Creedite

	Belyankite, Kazakhstan 1	Creedite			
		Colorado 2	Colorado 3	Bolivia 4	Calculated 5
CaO	34.00	33.57	35.18	34.7	34.17
Al_2O_3	21.88	21.89	21.42	25.9	20.71
SO_3	not det.	15.29	15.91	16.5	16.26
F	49.01	(30.35)	30.30	27.0	30.88
H_2O+	15.35	11.08	10.72	8.5	10.98
H_2O-	0.30	0.72	—	—	—
	120.54	112.90	113.53	112.6	113.00
O=2F	20.63	12.78	12.76	11.4	13.00
	99.91	100.12	100.77	101.2	100.00

1. M. O. Stepan, analyst, in Dorfman, 1950.
2. Recalculated. Wells, analyst, in Larsen and Wells, 1916.
3. Recalculated from Foshag, 1922.
4. Herzenberg, 1949.
5. Calculated for $Ca_3Al_2(SO_4)(F, OH)_{10} \cdot 2H_2O$, with F:OH=8:2.

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* Publication authorized by the Director, U. S. Geological Survey.

A comparison of the properties of belyankite, as given, with those of creedite leaves little doubt as to their identity. The analysis of belyankite is compared with the three analyses of creedite in Table 1. The method of analysis used for the Kazakhstan material is not stated; if sulfate was present but overlooked, it could affect the determination of of fluorine and water seriously. The analysis of belyankite gave determinations of CaO and Al_2O_3 very close to those reported for creedite.

Dorfman's drawing shows the narrow front pinacoid, *a*, which according to Foshag (Foshag, 1922) "sometimes occurs as a very narrow face . . . " on the crystals of creedite.

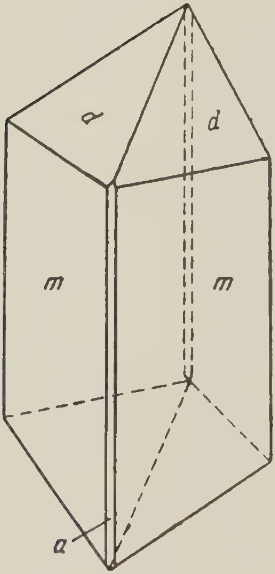

Fig. 1. Crystal drawing of belyankite, after Dorfman.

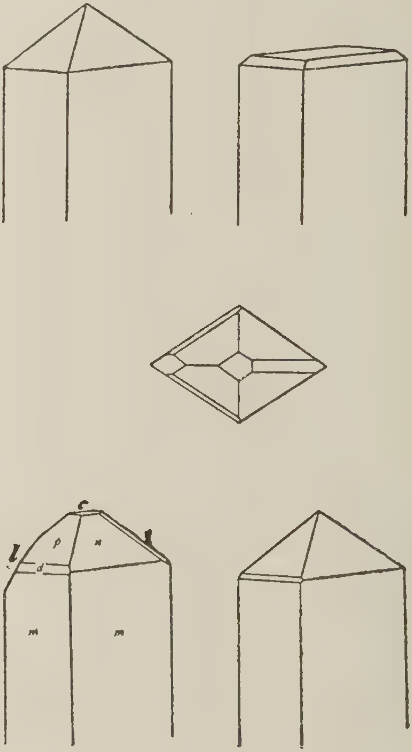

Fig. 2. Crystal drawings of creedite from Colorado after Foshag.

Dorfman does not give any goniometric measurements, but he quotes a determination of the unit cell constants, by S. S. Kvitka, as follows: $a_0=13.47\pm0.10$ Å., $b_0=8.46\pm0.05$ Å, $c_0=9.89\pm0.05$ Å, $\beta=93°\pm30'$. These yield the axial ratio $a:b:c=1.59:1.00:1.17$, $\beta=87°$, which agree closely with those given by Foshag for creedite, namely, $a:b:c=1.612:1.000:1.160$, $\beta=85\frac{1}{2}°$.

Other properties likewise are very close, as shown in Table 2. Dorfman's value for α is probably intermediate between β and the true α.

As neither x-ray powder data nor differential thermal analysis curves for creedite have been published, these were obtained on a sample, U.S.N.M. 93,117, from Wagon Wheel Gap, Colorado, part of the material studied by Foshag (Foshag, 1922).

The x-ray powder patterns were taken by F. A. Hildebrand with a North American Phillips Debye-Scherrer powder camera (114.59 mm. diameter), using the Straumanis technique and ethyl cellulose spindles with Cu K (Ni filter), λ-1.5418 Å. The data are given in Table 3 and although many lines measured on this film are not recorded by Dorfman, the agreement is good except for the six innermost spacings, missing from the data for belyankite. It was thought that the differences might be due to our having used a camera of 114.6 mm. diameter, whereas Dorfman's data were obtained with a camera of 57.3 mm. diameter. However, five of these six lines were still measurable on a film taken in this laboratory with a camera of 57.3 mm. diameter. A third photograph, taken with a camera of 57.3 mm. diameter with the beam catcher removed, gave a pattern with three of the six innermost spacings missing and the other three scarcely measurable, and it may be that this corresponds approximately to the conditions used by Dorfman. His data for gearksutite agree fairly well with those of Ferguson (Ferguson, 1949), but similarly show many lines missing.

TABLE 2. COMPARISON OF OPTICAL PROPERTIES OF BELYANKITE AND CREEDITE

	1 Belyankite, Kazakhstan	2 Creedite Colorado	3 Creedite Nevada
α	1.468	1.461	1.462
β	—	1.478	1.478
γ	1.483	1.485	1.483
Optic sign	neg.	neg.	neg.
2V	64°	64°	Med. large
Sp. gr.	2.720	2.713 2.720	—

1. Dorfman, 1950.
2. Larsen and Wells, 1916; Foshag, 1922.
3. Foshag, 1932.

A differential thermal analysis curve was kindly run on the Colorado creedite by Dr. G. T. Faust of this laboratory. His curve is reproduced in Fig. 4, that of Dorfman in Fig. 3. One of the two small exothermic reactions shown by the curve for the material from Kazakhstan is not present on the curve for creedite.

Belyankite occurs in veins associated with fluorite, kaolin, and pyrite in kaolinized granite adjacent to quartz-topaz greisen. Creedite at Wagon Wheel Gap, Colorado, is closely associated with fluorite and halloysite in a fluorite-barite vein; at Granite, Nevada, creedite is similarly associated with fluorite and halloysite in a gold-bearing vein.

Table 3. *X*-ray Powder Diffractiln Data for Creedite, Wagon Wheel Gap, Colorado (F. A. Hildebrand) and for Belyankite, Kazakhstan, (Dorfman)

Creedite		Belyankite		Creedite		Belyankite		Creedite		Belyankite	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7.3	9	—	—	2.19	6	—	—	1.439	2	1.433	w.
6.9	9	—	—	2.161	9	2.152	str.	1.418	1	—	—
5.79	8	—	—	2.103	4	—	—	1.407	1	—	—
4.98	6	—	—	2.062	2	—	—	1.390	1	—	—
4.18	4	—	—	2.023	5	2.025	str.	1.320	2	1.318	w.
4.08	4	—	—	2.002	3	—	—	1.283	4	1.282	w.
3.92	9	3.861	med.	1.975	4	—	—	1.256	1	—	—
3.67	7	3.652	w.	1.937	5	1.928	w.	1.245	1	—	—
3.48	10	3.430	str.	1.918	3	—	—	1.232	2	1.225	w.
3.27	7	3.245	w.	1.884	4	—	—	1.217	1	1.204	w.
3.07	8	3.039	med.	1.852	5	1.840	w.	1.189	1	—	—
3.01	4	—	—	1.817	1	—	—	1.178	1	—	—
2.98	4	—	—	1.789	1	—	—	1.159	3	—	—
2.90	5	2.876	w.	1.751	5	1.743	w.	1.156	1	—	—
2.82	4	—	—	1.711	1	—	—	1.143	1	—	—
2.76	7	—	—	1.678	3	1.677	w.	—	—	1.106	w.
2.71	7	2.709	med.	1.644	3	—	—	—	—	0.917	w.
2.61	6	2.602	w.	1.610	4	1.604	w.	—	—	0.882	w.
2.50	6	—	—	1.580	3	1.586	med.				
2.44	6	2.424	w.	1.547	1	—	—				
2.41	2	—	—	1.517	3	1.507	med.				
2.35	3	—	—	1.504	1	—	—				
2.32	5	2.300	v.w.	1.479	1	—	—				
2.29	6	—	—	1.457	1	—	—				

str. = strong, med. = medium, w. = weak, v.w. = very weak. *d* values are Ångstrom units; intensities are relative to the strongest line, taken as 10.

In summary, all lines of evidence point to the identity of belyankite with creedite, and indicate that its analysis is in error owing to the presence of sulfate having been overlooked. The possibility has been considered that belyankite is a sulfate-free creedite with perhaps an isomorphous series existing. The nearly perfect identity of properties is evidence against this rather unlikely hypothesis, but the question can be settled only by re-analysis of belyankite.

It should be noted that another mineral, also named for D. S. Belyankin, has recently been described under the name belyankinite (see p. 882). This hydrous calcium titanate should not be confused with belyankite.

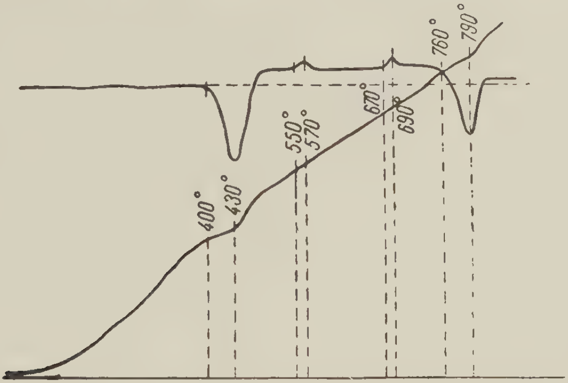

FIG. 3. Differential thermal analysis curve of belyankite (reproduced from Dorfman).

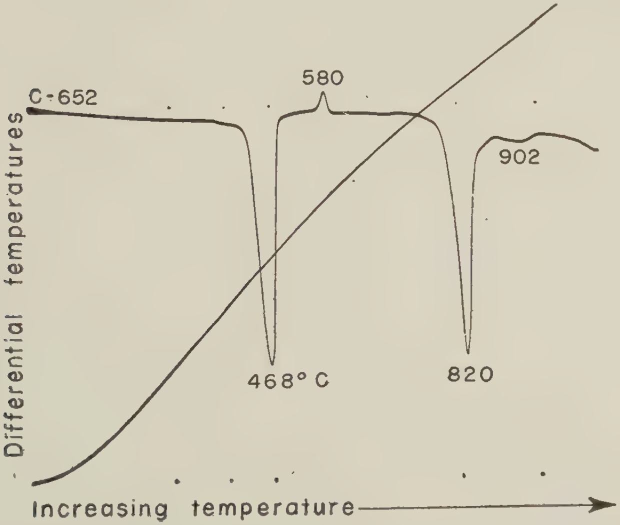

FIG. 4. Differential thermal analysis curve of creedite, Wagon Wheel Gap, Colo. Data of G. T. Faust.

It is obvious that my colleagues W. T. Schaller, F. A. Hildebrand, and

G. T. Faust have contributed practically all of the new data in this paper. As they decline to be co-authors of record, I can only thank them for their kind help. I also thank Dr. George Switzer of the U. S. National Museum, who furnished the creedite from Colorado.

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NEW METHODS FOR DETECTING CERTAIN CRYSTALLINE DEFECTS IN QUARTZ

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ABSTRACT

Two additional new methods were found for the detection of those crystalline defects in quartz, arising probably from submicroscopic inclusions, which have been detected by the writer's method of etching quartz with hydrofluoric acid under an alternating electric field. The first method consists of subjecting a quartz plate under investigation to the action of an electric discharge at low pressure, and then immersing it in hydrofluoric acid. The second method is simply to etch a plate by exposing it to the vapors of alkaline metals at about 350° C. In each case etching patterns were observed on most of the Z-section plates with the form of a system of polygons or zonal patterns similar in appearance, but not in their elementary constituent figures, to those produced by the method of etching under an electric field.

In the first method, four essential facts have been found: (1) the effect of an electric discharge as manifested by the persistency of the etching patterns is restricted to a certain depth of the superficial layer of the exposed surface, (2) this effect can be removed by heat treatment, (3) no etching patterns were produced on X-section plates, (4) dew patterns similar to etching patterns can be formed by condensing water vapor on the unexposed surface of a plate that has been newly subjected to the action of an electric discharge. Tentative explanations for the first three facts have been proposed and the reason for the fourth one requires further investigation.

INTRODUCTION

It was shown by the writer (1) that the application of a high alternating electric field normal to a quartz plate during etching with hydrofluoric acid results in the formation of two kinds of elementary etch figures. Figures of one kind differ from those of the other both in size and in structure. While the figures of microscopic dimensions are exactly the same as are those ordinarily found in etching under a non-electric field, those of visible size are produced only when there is an active electric field. (The former will subsequently be called the ordinary figures, and the latter the electric figures.) It was also shown that the electric figures (2), produced on plates cut from the so-called high grade crystals, are generally not distributed at random but are more concentrated in some regions than in others, forming a system of concentric polygons together with some special zones of irregular boundaries (in some cases only the zonal pattern is present). Furthermore, there is no such preferential distribution of the etch figures in the case of etching without an electric field. As previously remarked, the appearance of the polygonal and zonal patterns indicates the existence of two kinds of crystalline defects arising probably from submicroscopic inclusions. Subsequent work (3) on comparing the etching patterns of plates cut from the same blocks of quartz, proved conclusively that these defects are spatially distributed in a crystal. As a matter of fact, the appearance of the concentric polygonal patterns strongly reminds one of the annual rings of wood and it is fairly certain that this pattern indicates the contours of the crystal during early stages of its growth.

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* In previous publications the family name was placed first instead of last in accordance with the Chinese custom.

Regarding the polygonal etching pattern, mention should be made of the investigation of C. Frondel (4) on the coloring effect by x-rays on quartz. He showed that smoky bands having directions parallel to the rhombohedral faces of the mother crystal are sometimes developed in quartz plates by the application of x-rays. According to Van Dyke and Clyde P. Glover (5), the polygonal etching patterns produced by the writer's method and the colored patterns of Frondel are both formed in the same region of a given plate.

In view of the frequent occurrence of crystalline defects and also of their possible connection with the well-known variation of certain physical constants of quartz as previously indicated (2), it seemed worth while to see under what other conditions these defects could be detected. As a result of such an undertaking, two additional new methods were found; the one employing the combined action of an electric discharge and hydrofluoric acid, and the other to the corrosive action of the vapors of alkaline metals.

Experimental

The Z-section and X-section plates of a thickness varying from one to two millimeters were used throughout the work. The quartz plates used were either polished or smoothed with M303 emery as the case might require. As the techniques employed in the study of the effects on the crystalline defects of quartz by the electric discharge method and the action of the vapors of alkaline metals are different, they are described in the following under separate headings:

Method 1, By Means of the Electric Discharge

The discharge apparatus used resembled the ordinary sputtering type, of which the essential parts are diagrammatically shown in Fig. 1. A bell-jar about 20 cm. in diameter and 30 cm. in height was used as the discharge chamber. It rested on a thick iron platform, *D*, with its well-ground mouth sealed thereto with apiezon-sealing compound to make it air tight. The top opening of the jar was fitted with a brass stopper, through which an aluminum rod, *A*, was passed, the joints being made air-tight also with apiezon-sealing compound. A circular aluminium plate, *P*, used as the upper electrode of the discharge system, was attached to the lower end of *A*. A flanged aluminum disk, *F*, attached to a massive brass cylinder served as the lower electrode. The quartz plate, *Q*, to be investigated was placed on the disk. For a reason to be pointed out later, *Q* was not to rest directly on the disk, but separated by about 0.2 mm. by means of three small supporting slats, *R*. The massive lower electrode possessed large heat capacity which prevented the temperature of the plate, *Q*, from rising dangerously high during discharge. To prevent stray discharge, the brass cylinder, *E*, and the part of the rod, *A*, inside the jar were sheathed with glass tubings G_2 and G_1, respectively. In order to render the electric field over the quartz plate as uniform as possible, the distance between the two electrodes

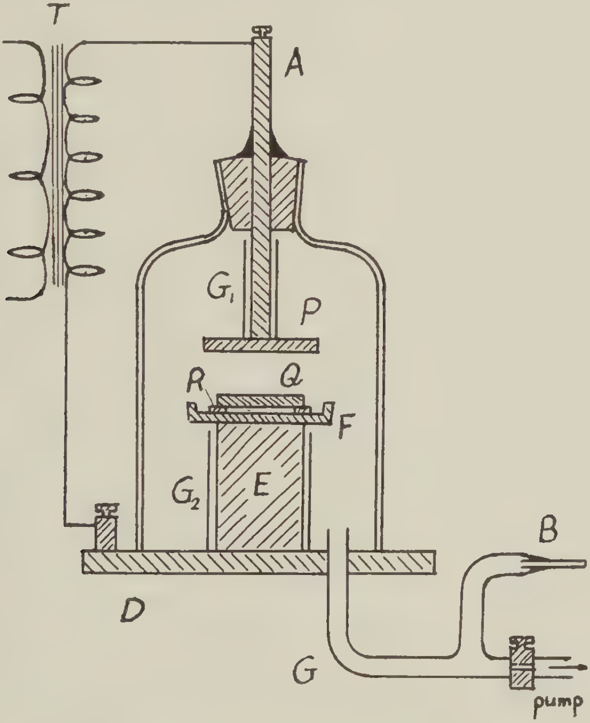

FIG. 1. Discharge apparatus. *P*, upper electrode; *F*, lower electrode; *Q*, quartz plate; *R*, supporting slats of *Q; E*, massive brass cylinder; *D*, iron platform; *B*, palladium tube; *T*, transformer.

was constantly kept smaller than either of the diameters of the two electrodes. Through the glass tubing *G*, the discharge chamber was connected to an evacuating system (not shown), which consisted of an oil pump and a mercury diffusion pump. The pressure of discharge was measured by means of a McLeod gauge. A palladium tube, *B*, attached to *G*, permitted the introduction of pure hydrogen into the discharge chamber in case of necessity. High tension used in the discharge was supplied by a 10,000-volt transformer. The alternating voltage across the electrodes during discharge was about 700 volts and the current passed through was about 3 milliamperes. The duration of discharge varied from half an hour to a score of hours, as required by the tests.

When the discharge was over, the quartz plate, *Q*, was taken out of the jar and ready for any one of the following investigations:

(1) To study the effect of discharge on the etching of quartz by plunging the plate into hydrofluoric acid for a specified time.
(2) To see how the temperature would influence the effect of discharge by heating the plate to about 300° C. in an electric furnace for about half an hour before plunging it into hydrofluoric acid.
(3) To study the effect of discharge on the condensation of water vapor on the plate surface.

In performing the second investigation, the quartz plate was cut into two pieces; one of them being then introduced into a furnace and the other kept at room temperature. When the heating operation was over, the two pieces were simultaneously plunged into hydrofluoric acid. Then a comparison was made of their etched surfaces. As for the third investigation, the water film might be conveniently produced by condensing the vapor in the moist air from the mouth.

Method 2, By Means of the Vapors of Alkaline Metals

The vapors of sodium, potassium, and rubidium were used as the etching agents for quartz. A small capsule of an alkaline metal, together with one or several pieces of quartz plates to be investigated, were introduced into a large Pyrex tubing one end of which had been sealed. The tubing was then connected to an evacuating system. After evacuation and sealing the tubing was placed in a cylindrical electric oven for heating. The alkaline metals begin to vaporize appreciably at 150° C., as could be judged from the coloration of the tubing. But in order to obtain good etched plates it was found necessary to raise the temperature to about 350° C. and to maintain it there for three or four hours. When the etching process was over, the plates were taken out and rinsed with fresh water to remove a layer of colored coating formed on them during etching.

RESULTS

Part 1, Effect of an Electric Discharge

Quartz plates having been subjected to the action of an electric discharge for several or even a score of hours, undergo no apparent changes other than the addition of an almost invisible metallic film on their exposed surfaces. (By exposed surface is meant the surface facing the upper electrode, *P*.) However, when they are immersed in hydrofluoric acid, the etching patterns take the form of a system of concentric polygons and special zones with irregular boundaries are developed on the exposed surfaces of most of the Z-section plates but never on their unexposed surfaces. These patterns are identical in form with, but different in their elementary constituent figures from those produced by etching under an a.c. electric field. In fact, the former are composed of the ordinary pyramidal figures which are the usual characteristic etch figures of the *Z*-section, while the latter are composed of star-shaped electric figures. Moreover, in contrast to the figures obtained by electric discharge, the ordinary figures in the polygonal and zonal patterns do not appear to be concentrated in certain regions. Microscopic examination has revealed that in these patterns, the average size of the ordinary figures as well as their number per unit area, are somewhat smaller than those in the other part of the same etched surface. This fact indicates that electric discharge brings about a difference in rate of dissolution of quartz between regions containing submicroscopic inclusions and those free from them. Since the difference both in size and in number of the etch figures in the different regions is small, the visibility of the patterns by electric discharge is generally low, in fact too low to be reproduced photographically. It is to be pointed out that under similar experimental conditions, no etching patterns of a similar nature can be produced on X-section plates.

In regard to the pattern-producing effects of electric discharge, there are several related phenomena which deserve mentioning. First, this effect as manifested by the persistency of the polygonal and zonal etching patterns was found to reach in some cases a depth of about 0.03 mm. In other words, the etching patterns continue to exist until the pattern-bearing superficial layer was dissolved by the corrosive acid. The depth of the affected layer does not depend appreciably upon the duration of discharge from some thirty minutes upwards, nor upon the kind of gas (air or hydrogen) used in the discharge. It may be of interest to remark that the pattern depth of 0.03 mm. is about three times the average height of the pyramidal etch figures of which the patterns are composed. The above mentioned fact tends to show that the depth of the affected layer represents the penetrating range of some sort of moving particles. Second, the visibility of the etching patterns was found to depend markedly upon both the pressure of the discharging gas and the orientation of the quartz plate during discharge. Other things being equal, the optimum pressure for obtaining patterns of high visibility lies between the interval of 0.2 to 0.5 mm. of mercury. For pressures higher than 0.8 mm. or lower than 0.01 mm. the pattern-producing effect vanishes. For unknown reasons it was found necessary to separate the plate and the lower electrode by a distance of some 0.2 mm. Third, the pattern-producing effect acquired by a plate during discharge is removable by heat treatment. This is conveniently shown by heating a plate having been subjected to discharge, in an electric furnace before etching. Such a plate loses the said effect slowly at 150° C. and very quickly at 300° C. or higher. Also, the method of electric discharge furnishes another rather peculiar way for detecting the defects of quartz. When water vapor is made to condense on the unexposed polished surface of a plate freshly stimulated by discharge, polygonal and zonal patterns will be formed on the dew film in case this plate does possess the corresponding defects. The appearance of the dew patterns is similar to the etch patterns which are produced, as pointed out in the foregoing paragraph, on the opposite face, i.e., the exposed surface, when the plate is treated with hydrofluoric acid. Owing to the rapid evaporation of such a dew film, it has not been possible to examine microscopically the size and the manner of distribution of the droplets in the different parts of the film. Patterns of this kind can be reproduced several times after each evaporation; but if the surface is touched with a finger, or a moistened cloth, the peculiar phenomenon disappears. No such patterns have ever been observed on the exposed surface of the same plate. For the observation of dew patterns, a polished surface was found to be indispensable.

Part 2, Effect of Alkaline Metals

The vapors of alkaline metals were found to etch quartz quite perceptibly at about 150° C. The etching becomes more and more vigorous as the temperature rises. However, owing to the formation of a superficial layer of non-volatile material which prevents rather effectively the contact between the surfaces and the metallic vapors, the etching process soon slows down. A well etched plate may be obtained by raising the temperature to about 350° C. and at the same time prolonging the etching duration to several hours. The increase in etching by extending the duration beyond one or two hours appears to be practically negligible.

Figure 2 is a photomicrograph of the etch figures produced by potassium vapor on a Z-section plate. As may be seen the etched face is granulated. Among the granular figures also some curved grooves may be noted. The etching produced by the different metallic vapors are similar. These granular etch figures bear no resemblance to the pyramidal ones produced with hydrofluoric acid.

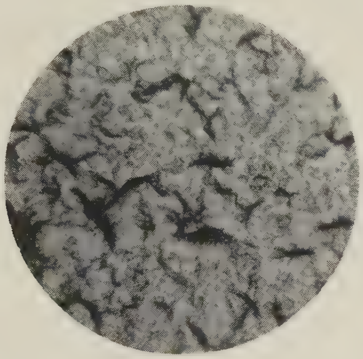

FIG. 2. Etch figures produced by potassium vapor. Magnification 100×.

The main object of this part of the work was to see whether it was possible to detect the defects of quartz by using the etching power of vapors of alkaline metals. The result is affirmative. The appearance of the polygonal and zonal etching patterns caused by the vapors of these metals is similar to those produced by other methods mentioned above. The visibility of these etching patterns is generally low. Considering the three metals used in the experiments, namely sodium, potassium and rubidium, the third is not as effective as the other two in that the colored layer on the plate is insoluble not only in water but also in other cleaning solvents.

DISCUSSION AND CONCLUSION

As is conceivable, when a quartz plate is exposed to electric discharge, it is actually subjected to three types of actions, namely, the irradiation of ultraviolet and visible radiations, the action of an electric field, and the bombardment of speedy particles. Evidently the cause of the pattern-producing effect of an electric discharge must be sought for among these actions. In view of the fact that the form of the ordinary etching figures and the rate of dissolution of quartz in hydrofluoric acid can both be greatly modified by the action of ultraviolet radiations (6), attempts have therefore been carried out to reproduce the etching patterns similar to those by an electric discharge by irradiating the Z-section plates with an intense iron-spark, either before or during etching. However, the result was negative. The fact that an alternating electric field can produce polygonal and zonal patterns when, and only when, the field is applied to quartz during etching with hydrofluoric acid, discards the possible role of the second action. Hence the responsibility for the specific effect falls exclusively on the bombarding action of speedy particles. Since a speedy particle may penetrate a substance to a certain depth before being stopped, the existence of a superficial layer of the order of 0.03 mm. in thickness and with the polygonal and zonal etching patterns continuing to exist therein, seems to offer a strong support to the third hypothesis. However, a quantitative consideration of the problem will show that the bombardment hypothesis is not as readily acceptable as it may appear to be at first sight. Statements in the subsequent paragraphs will make this point clear.

Since the speedy particles must derive their kinetic energy from the discharging circuit we may first assume these particles to be ionic in nature and then test the validity of the bombardment hypothesis. This can be done by estimating the kinetic energy necessary for an ionic particle to penetrate to a depth of 0.03 mm. into the quartz on the one hand, computing the maximum kinetic energy attainable by it in the discharged circuit on the other hand, and then comparing the magnitude of these two quantities. It is possible to attain this end by resorting to a rather roundabout way. Let us estimate the range of an alpha particle in quartz. The stopping power, S, of a molecule of a given substance is known and can be expressed as

$$S = \frac{R_0 d_0}{Rd} \frac{M}{A_0} \tag{1}$$

where R_0 and R represent the ranges of an alpha particle in a standard gas and in the given substance, respectively, d_0 and d, their densities, A_0 the atomic weight of the gas and M the molecular weight of the substance. According to Bragg and Kleeman, the stopping power of an atom is proportional to the square root of its atomic weight and the relative molecular stopping power may be obtained by adding together the stopping powers of the constituent atoms. Hence the molecular stopping power of quartz can be written as

$$S = [(28)^{1/2} + 2(16)^{1/2}]k = 13.3k \tag{2}$$

where k is a constant of proportionality. The value of k is 0.27 as deduced from the known ranges of the alpha particles of RaF both in air (standard gas) and in oxygen by means of eq. (1) and the law of Bragg and Kleeman. Hence the value of S in eq. (2) is equal to 3.59. By taking air at normal conditions as the standard gas and quartz as the given substance and substituting the proper physical constants in eq. (1), the relation between the range of alpha particles in quartz, R, and that in air, R_0, becomes:

$$R = 0.0005R_0. \tag{3}$$

The variation of the kinetic energy of a charged particle along an element dx of the trajectory in quartz may be expressed by a formula according to Bethe (7), which is (for a constant mass of the particle):

$$\frac{dW}{dx} = -\frac{4\pi Z^2e^4Nn}{mv^2}\log_e\frac{2mv^2}{F} \tag{4}$$

in which W represents the kinetic energy of the moving particle: Ze, its charge; v, its velocity; N, the number of electrons per molecule of quartz; n, the number of molecules per cm^3; m, the mass of an electron; and F, the geometrical mean of the energies of excitation and ionization of the molecule. Upon substituting W by its equivalent $\frac{1}{2}Mv,^2$ where M represents the mass of the moving particle, and integrating the resultant expression, the length of the trajectory, i.e., the range, R of the particle is found to be

$$R = \frac{Mm}{4\pi Z^2e^4Nn}\int_0^v \frac{v^3}{\log_e\dfrac{2mv^2}{F}}dv \tag{5}$$

For brevity, let

$$\phi = \int_0^v \frac{v^3}{\log_e\dfrac{2mv^2}{F}}dv,$$

then

$$\phi = \frac{4\pi Z^2e^4Nn}{Mm}R. \tag{6}$$

It is to be noted that for a given stopping medium, ϕ is independent of the kind of moving particle but is a function of its velocity alone. Since the value of F for a quartz molecule is not known, the ϕ cannot be evaluated directly from the integral; but it can be deduced from eq. (6) if the various quantities on the right-hand side of this equation are known. Now the ranges in air, R_0 of alpha particles are known for their various kinetic energies, E, so their ranges in quartz, R, and hence the corresponding values of ϕ can be calculated by eq. (3) and (6), respectively. Some of such data on the alpha particles are tabulated in Table 1. Figure 3 is obtained by plotting E taken from the second column of Table 1 as abscissae and ϕ of the fourth column as ordinates. As may be seen from the curve, the E-ϕ relationship is approximately a linear one, and the curve on being extended, passes through the origin. Later

TABLE 1. DATA ON ALPHA PARTICLES. R_0 REPRESENTING THE RANGE OF ALPHA PARTICLES IN AIR; R, THE RANGE IN QUARTZ; E, THE KINETIC ENERGY OF THE PARTICLES EXPRESSED IN ELECTRON-KILOVOLTS; AND ϕ, THE VALUE OF THE CORRESPONDING VELOCITY FUNCTION

*R_0 (cm)	*E (in electron kilo-volts)	$R\times10^{-4}$ (cm)	$\phi\times10^{-35}$
0.55	1167	2.9	1.09
0.62	1328	3.3	1.23
0.70	1499	3.8	1.39
0.80	1681	4.3	1.59
0.91	1873	4.9	1.80
1.04	2075	5.6	2.07

* Data cited from Madame P. Curie, (Radioactivity) Radioactivité, Hermann & C^{ie}, Paris, 1935, p. 530.

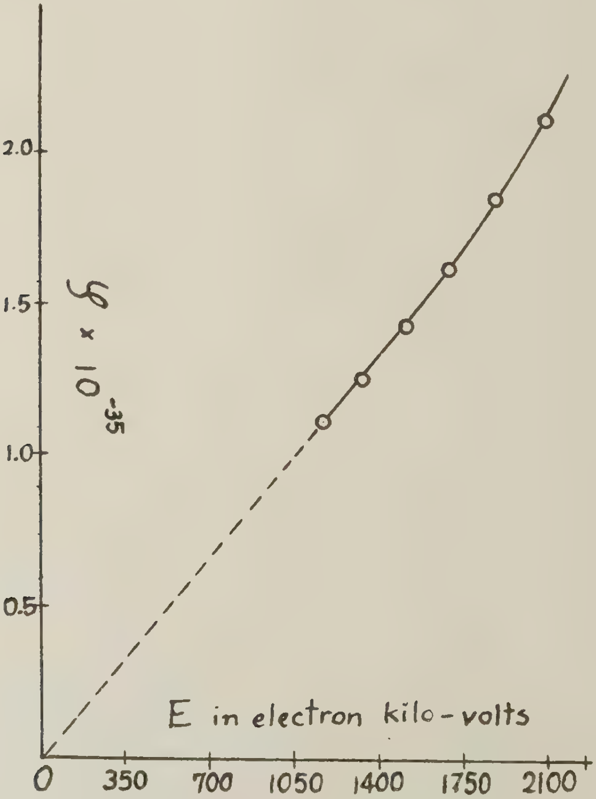

FIG. 3. E representing the kinetic energy of alpha particle, ϕ the corresponding velocity function.

on use will be made of the accompanying figure for estimating the kinetic energies of ions other than the alpha particles.

As is conceivable, molecular ions as well as free electrons will coexist in an electric discharge. These ionic particles will be accelerated by the discharged electric field and may thus attain high speeds. Moreover, as may be inferred from existing spectroscopic data, practically all the charged particles present under the specific discharged conditions are singly ionized. For this reason, Z may always be set to unity in the calculation of ϕ from eq. (6). Consider first, the case of singly ionized molecules of oxygen which should be the heaviest ions in the air under discharge. If the depth of the layer in which the polygonal and zonal etching patterns persists is taken as the penetrating range of a diatomic oxygen ion, the value of ϕ, as calculated from eq. (6) is 0.33×10^{35}. The kinetic energy, E of an alpha particle corresponding to this value of ϕ, is found by extrapolating the curve of Fig. 3 to be about 350 electron-kilovolts. Since charged particles of different kinds, possess the same speed for a given value of ϕ, the ratio of the kinetic energy of one kind of particle to that of the other is the same as the ratio of their masses, i.e.,

$$\frac{E_1}{E_2} = \frac{M_1}{M_2} \tag{7}$$

where E_1 and M_1 represent the kinetic energy and mass, respectively, of one kind of particle and E_2 and M_2 the corresponding quantities of the other kind. Hence the kinetic energy of a singly ionized oxygen molecule having a range of 0.03 mm. in quartz is found to be 2800 electron-kilovolts. On the other hand, if a free electron is taken as the particle which has a penetrating range of 0.03 mm. in quartz, the corresponding value of ϕ will be 1.92×10^{39}. By supposing the linear relationship in Fig. 3 to be still valid for a value of ϕ as large as 1.92×10^{39} and making use of eq. (7), a rough estimate of the kinetic energy of the penetrating electron is possible. The result so obtained is about 2400 electron-kilovolts. For ions with masses intermediate between the mass of an electron and that of a diatomic oxygen molecule, the kinetic energies will be lying within the interval between 2400 and 2800 electron-kilovolts.

The maximum kinetic energy acquirable by a charged particle in an electric discharge may be estimated from the conditions of discharge. Take for example the case of a discharge in air under a pressure of 0.2 mm. Hg, which is the lower limit of the optimum pressure of discharge for obtaining etching patterns of high visibility. At this pressure, the mean free path of an oxygen molecule is about 0.035 cm. and that of an electron, 0.18 cm. The cathode fall of potential for air is known to be around 340 volts and the anode fall of potential some 20 volts. Hence the maximum kinetic energy of a positive oxygen molecule (O_2^+) will be of the order of 66 electron-volts and that of an electron much less. For any other kind of ions, the mean free path will be somewhat greater or smaller (for example N_2^+) than that of a diatomic oxygen molecule and so will be the kinetic energy. But in every case, the maximum kinetic energy acquirable is more than thirty thousand times smaller than that demanded by the range-velocity relationship. This discrepancy appears to be a serious blow to the bombardment hypothesis under discussion. However, the difficulty is reconcilable by postulating that the effect of discharge on the formation of etching patterns is due to the action of speedy neutral molecules rather than to that of ions; for if Z of eq. (5) which represents the number of the electronic charge of the moving particle, is set at zero, the range R becomes infinite, theoretically. It is very probable that for a neutral particle to be able to penetrate into a solid medium, a minimum kinetic energy is necessary. The energy thus required can be drawn from a speedy ion by the process of collision. Moreover, a speedy ion may also be transformed directly into an energetic neutral one by neutralization.

The statement of the foregoing paragraph indicates that gaseous molecules are liable to be embedded in the superficial layer of a Z-section plate through the process of an electric discharge. On the other hand, it was suggested by the writer that the regions in which the polygonal and zonal etching patterns are found, are the sites of submicroscopic inclusions. According to the quantum mechanical theory of solids the electron energy levels are grouped into quasi-continuous bands separated by gaps of the order of a few electron-volts in width. When foreign molecules are inserted into the lattice they may give rise to localized energy levels within the gaps between energy bands of the base materials. Hence it is reasonable to postulate that for a quartz plate having been subjected to the action of an electric discharge, the localized energy levels created within the gaps of bands will be different between the regions containing submicroscopic inclusions and those free from them. This eventual difference in energy levels might give rise to unequal rates of dissolution of quartz by hydrofluoric acid and thus render the specific regions discernible. That the pattern-producing effect of discharge can be removed by heat treatment is also comprehensible; since vigorous thermal agitation may help the embedded gaseous particles to diffuse away.

The fact that an electric discharge has no pattern-producing effect on X-section plates, might have something to do with the piezoelectric property of quartz. Indeed it seems sound to suppose that for a X-section plate, free charges are liable to be created on the spot of bombardment of a speedy particle and that part of these charges may attach to the bombarding particle, thus rendering the penetrating power of the particle negligibly small.

The feasibility of obtaining dew patterns, similar to etching, by condensing water vapor on the unexposed surface of a newly stimulated Z-section plate is something rather peculiar. In view of the fact that this peculiar effect of an electric discharge is easily removable by touching the surface with a moistened cloth or a finger, it must be in some way connected with electricity. For a better understanding of this phenomenon, further investigation is undoubtedly necessary.

Prior to the present work, the crystalline defects of quartz have been detected most readily by the electric method of etching and less readily by the x-ray method. To these, two more methods may now be added, namely, the method of an electric discharge and that of etching by means of the vapors of alkaline metals. Of the four methods, the first appears to be most sensitive.

In conclusion, the writer wishes to acknowledge the helpful assistance of Mr. C. Y. Ling in drawing the diagrams, and of Mr. K. Y. Chou of the Zoology department for the photomicrograph shown in this paper.

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DIFFERENTIAL THERMAL STUDY OF COLORADO OIL SHALE*

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Abstract

Differential thermal curves of selected Colorado oil-shale samples showed endothermic dips in the temperature range of 450° to 475° C. These characteristic dips occurred within the temperature range of the conversion of organic material (kerogen) in oil shale to oil, gas, and organic residue. However, it is not known whether the dips resulted from heat absorbed in the vaporization of reaction products or possibly from endothermic reaction of kerogen. The thermal curves also showed the presence of calcite and/or dolomite but did not indicate the presence of clays.

Introduction

The method of differential thermal analysis, as suggested by Le Chatelier (7) in 1887, has undergone considerable development in recent years and emerged as an important means of studying the constitution of various substances. The theory of this analysis has been explained and applied by many investigators, such as Insley and Ewell (5), Norton (8), Hendricks *et al.* (4), Grim and Rowland (3) Speil (9), and Kerr and Kulp (6). Results obtained by most of these workers have shown that this method of analysis is especially valuable in the study of clay minerals.

In 1942 a similar technique of analysis was employed by Cane (2) of Australia to study torbanite, a rich oil shale. The investigation was concerned with the thermochemical properties of torbanite rather than its mineral constituents. In 1951, Sohns, Mitchell, Cox, Barnet, and Murphy (9) measured the heat requirements for retorting different grades of Colorado oil shale. They determined the over-all heat necessary to produce shale oil and accompanying byproducts under conditions that would exist in commercial practice. The data indicated that little heat was consumed in the conversion reaction; most of it appeared as sensible heat in the spent shale and retort products.

The investigation discussed herein is an application of differential thermal analysis to Colorado oil shale. Its purpose was to determine whether or not any mineral constituents, especially clays, could be identified in the oil shale and to determine the types of thermal reactions taking place during pyrolysis of the organic constituent of the shale.

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* Abridged from a M.S. thesis, "A Differential Thermal Study of Selected Colorado Oil Shales," University of Wyoming, 1948.

APPARATUS

The apparatus used in this study was patterned, in general, after Berkelhamer's design (1). A potentiometer was used in place of a reflecting galvanometer-photographic recorded arrangement, and a manually operated variable transformer was used in place of a motor-driven transformer. In brief, the equipment consisted of a tubular furnace, sample block and holder, thermocouples, two potentiometers, and a variable transformer.

One potentiometer recorded the differential temperature while another recorded the sample block temperature. Thermocouples were made of chromel-alumel wire (B&S gage No. 20). It was important that the size of the thermocouple hot-junction beads be uniform to prevent any effect on the slope of the base line of the thermal curves. To make smooth beads of approximately the same size, the thermocouples were dipped in flux and arc-welded with an apparatus consisting of two carbon rods and a small variable transformer. A uniform heating rate of about 11° to 12° C. was maintained during a run by manually changing the voltage setting of the variable transformer.

SAMPLES USED

Six Colorado oil-shale samples were selected to represent the types of oil shale being mined at the Bureau of Mines Oil-Shale Mine, near Rifle, Colorado. All of these samples were assayed according to the modified Fischer-retort method (10) to determine their oil yields. The oil yields, shown in Table 1, indicate the relative amount of organic material present in each sample, as it is this material that is converted to oil and gas upon heating.

TABLE 1. OIL YIELD OF OIL-SHALE SAMPLES

Sample designation[a]	Oil yield (Gal./ton)
A	2.2
B	10.5
C	26.7
D	36.3
E	61.8
F	75.0

[a] Detailed analyses of five of these samples (B through F) are available in *Bureau of Mines Report of Investigations* 4825, (1951), Properties of Colorado Oil Shale, by K. E. Stanfield, I. C. Frost, W. S. McAuley, and H. N. Smith.

Other samples included in this study were quartz and various known mixtures of kaolinite, calcite, and dolomite with oil shale.

THERMAL EFFECT OF ORGANIC MATERIAL IN OIL SHALE

Differential thermal curves[1] (Fig. 1) of the oil-shale samples studied indicated the effect of shale pyrolysis. Each thermal curve showed an endothermic dip, the peak of which occurred in the temperature range 450° to 475° C. This dip, which was proportional to the amount of organic material in the sample, was attributed to absorption of heat by vaporization of the conversion products or possibly to absorption of heat by the organic material (kerogen) of the oil shale. The conversion of organic matter to volatile products during a run was noted by the evolution of smoke, starting at 375° to 400° C., and continuing to about 500° C.

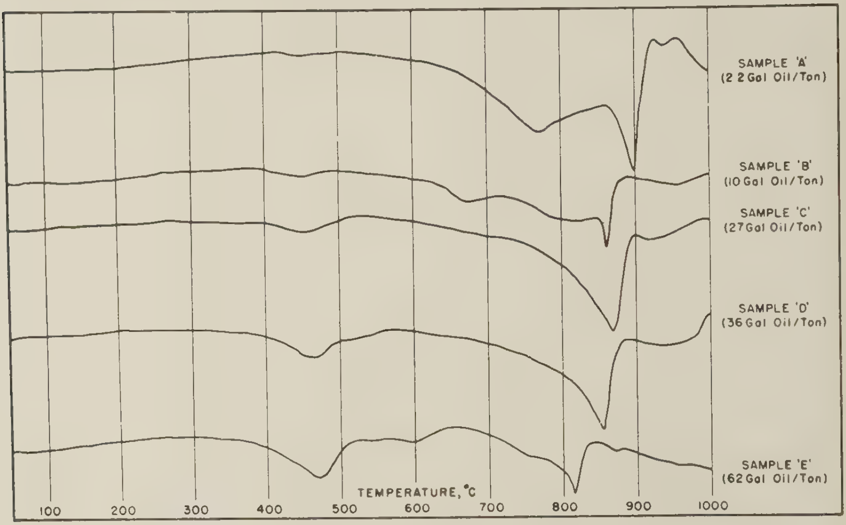

FIG. 1. Thermal curves of Colorado oil shales.

The thermal curve for sample *F* was not included in Fig. 1. To obtain a representative curve, it was necessary to mix an inert substance with this sample because the organic content of the sample was so high that, during a thermal run, the sample expanded, raising the cover of the sample block.

As was mentioned in the introduction, Cane applied this method of analysis in a study of Australian torbanite. In Cane's apparatus, two silica tubes were placed in a furnace, and thermocouples were placed in the tubes so as to constitute a differential thermocouple. One tube was packed with dehydrated fuller's earth and the other with dry powdered torbanite. The thermal curve reported by this method indicated the reaction to be irregular; that is, it showed both endothermic and exothermic reactions. In the temperature range 360° to 400° C., the curve showed a marked exothermic reaction that was attributed to decomposition of sulfur- and oxygen-containing compounds. The curve also indicated an endothermic reaction for decomposition of the organic matter.

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[1] Similar curves were obtained by the Bureau of Mines Station, Tuscaloosa, Ala., for samples E and C shown in Fig. 1, using a galvanometer-recorder type apparatus with a resistance of 600 ohms.

The thermal curves in Fig. 1 do not indicate an exothermic reaction as found by Cane. This difference in curves could possibly be due to differences in the samples or in the analysis technique.

Identification of Minerals in Oil Shale

According to a communication from T. A. Klinefelter, former mineral technologist, Bureau of Mines, Tuscaloosa, Ala., many oil shales contain illite and kaolinite. The thermal curves of Fig. 1 do not indicate the presence of either of these clay minerals. The presence of kaolinite in the shale samples would have been indicated because of its large thermal reactions. It can be seen from the thermal curves of kaolinite-oil-shale mixtures in Fig. 2 that, although the characteristic endothermic peak of kaolinite shifted to the left (lower temperature) as the percentage of kaolinite was decreased, it was still possible to detect the presence of small amounts of kaolinite. However, illite clay could have been present in appreciable quantity and yet not have been detected owing to lack of sensitivity of the apparatus. This sensitivity, as revealed by direct

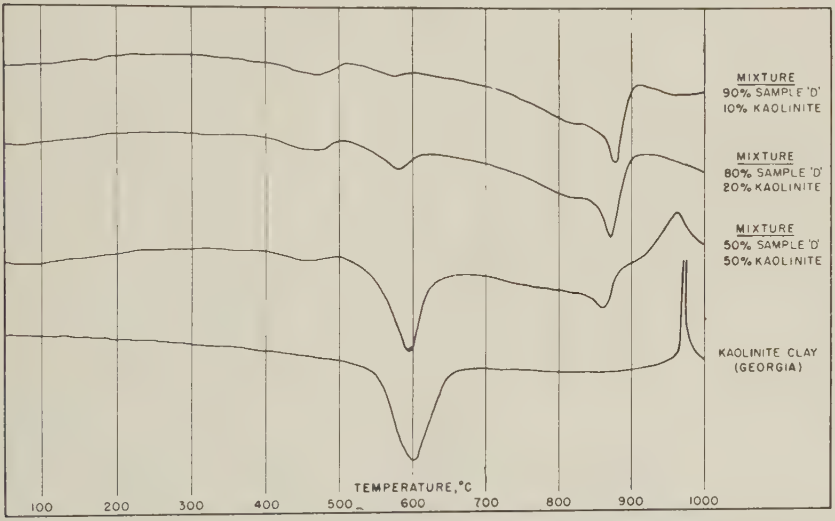

FIG. 2. Thermal curves of mixtures of oil shale and kaolinite clay.

potentiometer readings, was sufficient to detect small thermal changes in which the reaction was of short duration. For example, the alpha-beta inversion of quartz, which occurred suddenly at about 572° C. (Fig. 3), was readily indicated by a differential potential of between 0.05 to 0.08 millivolt (about 1° to 2° C.). However, for thermal changes of this same order of magnitude wherein the reactions occurred gradually, as in illite clay, the sensitivity proved to be insufficient.

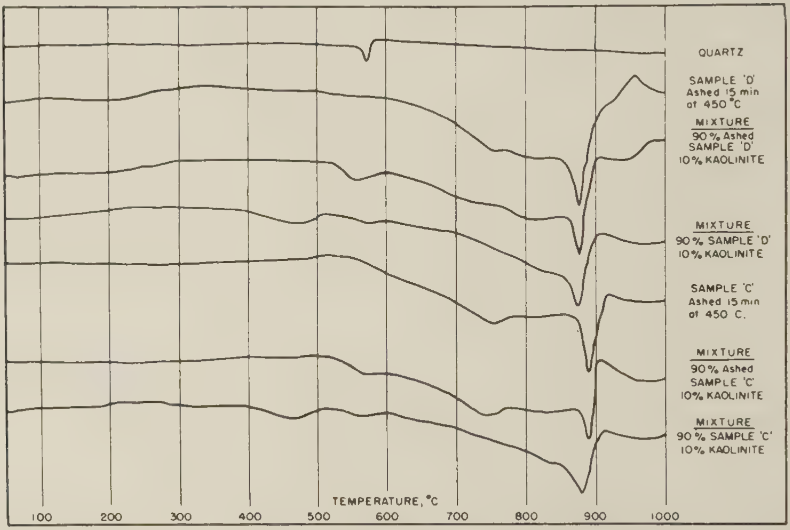

FIG. 3. Thermal curves of quartz and of mixtures of ashed oil shales and kaolinite clay.

The effect of decomposition of organic matter upon the identification of the clays in oil shale was studied. Two samples, *C* and *D*, were ashed 15 minutes in an open dish at 450° C. to burn off the organic matter, and runs were made on this ashed material, on mixtures of kaolinite and the ashed material, and on mixtures of kaolinite with the original shale. Thermal curves, Fig. 3, indicated a kaolinite dip in the temperature range of 550° to 580° C. for all the mixtures. Larger endothermic dips were obtained for the kaolinite-ashed shale mixtures than for the kaolinite-raw shale mixtures. This indicated that decomposition of the organic matter had an over-all effect of changing the thermal characteristics of any clays present in the oil shale.

On all the thermal curves in Fig. 1, an endothermic dip attributed to the presence of some form of carbonate was shown in the temperature range 800° to 900° C. The curves for samples *B*, *C*, and *D* showed an endothermic dip at about 850° to 875° C., which is characteristic of calcite. The curve for sample *E* showed an endothermic dip at about

820° C. A thermal curve for a mixture of this sample with 5 per cent calcite, Fig. 4, showed a larger dip at about the same temperature which suggested that the thermal peak at 820° C. for sample *E* was due to calcite. Similarly, curves for mixtures of sample *A* with calcite and dolomite, Fig. 4, suggested that the endothermic dip at about 770° C. was due to dolomite and that the endothermic dip at about 900° C. was due to dolomite and/or calcite.

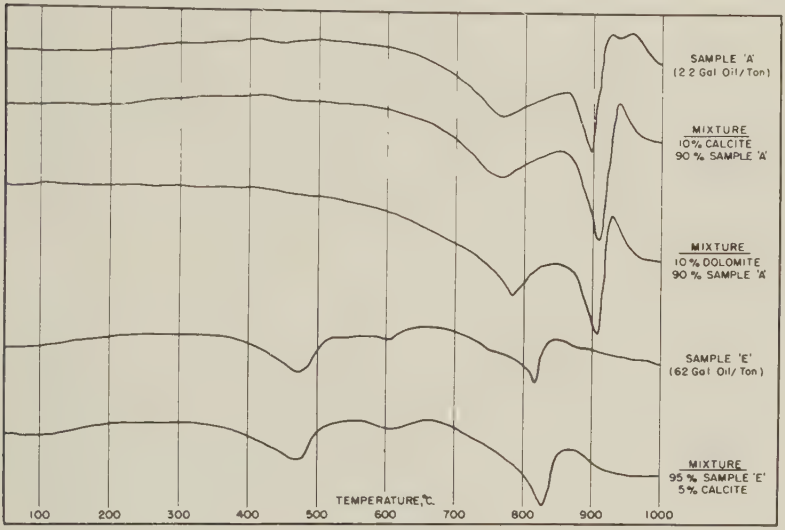

FIG. 4. Thermal curves of mixtures of oil shales and carbonates.

Petrographic analyses showed the presence of both dolomite and calcite in all the oil-shale samples. However, only the thermal curve for sample *A* clearly indicated the presence of dolomite. Sample *E* showed a slight dip characteristic of dolomite. A possible explanation of this is offered by use of the data in Table 2, which shows analyses of the oil-shale samples for magnesium and calcium content. The magnesium content of sample *A* was considerably higher than that of the others, which indicated the presence of more dolomite. In samples *B*, *C*, and *D* a large amount of CaO was shown, so it seems likely that the endothermic reaction due to calcite in these samples was sufficient to absorb completely the first dolomite dip occurring at about 770° C. In sample *E* less CaO was present, and the intensity of the calcite reaction was insufficient to absorb completely the first dolomite dip. It can be seen from the curves in Fig. 4 that the increased endothermic reaction due to the addition of 5 per cent calcite blocked out the small dolomite dip shown on the curve for sample *E*.

Table 2. Partial Chemical Analysis of Six Oil-Shale Samples

Sample designation	MgO per cent	CaO per cent
A	9.53	16.35
B	5.37	11.35
C	5.30	17.49
D	5.61	14.20
E	4.48	8.26
F	4.15	8.45

To supplement the differential thermal analyses, *x*-ray diffraction analyses were made of the six oil-shale samples. The following minerals were identified in all the samples: Quartz, calcite, dolomite, pyrite, illite clay, feldspar, and analcite. Only a small amount of illite clay, probably less than 10 per cent, was indicated.

Conclusion

Differential thermal analyses of six Colorado oil shales showed that: (1) An endothermic dip occurred within the thermal conversion range (450° to 475° C.) of kerogen to gas, oil, and organic residue, but it was not determined whether the conversion reaction was endothermic in character or whether heat was absorbed in the vaporization of the conversion products. (2) The decomposition of the organic matter affected any clays present in such a way that the magnitude of their characteristic thermal peaks was decreased. (3) Clays present in oil shale were not identified. (4) Carbonates, calcite, and/or dolomite, were present in all the samples studied.

X-ray analysis indicated the presence of a small amount of illite clay in all of the oil-shale samples. The combination of two factors—the effect of the decomposition of organic matter and insufficient sensitivity of the apparatus - prevented the identification of the illite clay by differential thermal analysis.

Acknowledgment

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Station, Tuscaloosa, Alabama, for checking thermal analyses of two samples; to H. N. Smith, Petrographer, Bureau of Mines, for the petrographic analyses and for assistance on *x*-ray analysis work; and to Irving C. Frost, Chemist, Bureau of Mines, for the chemical analyses.

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CELL SIZE, OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF LAUMONTITE AND LEONHARDITE

WITH A NOTE ON REGIONAL OCCURRENCES IN NEW ZEALAND

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ABSTRACT

Laumontite is found to be a large-scale replacement product of vitric tuffs in Southland, New Zealand, and a degradation product of plagioclase under incipiently metamorphic conditions. The well-known partial dehydration of laumontite to yield leonhardite is readily reversible, and optical and x-ray data are presented. Cell constants of leonhardite from Hungary are as follows: $a = 14.75 \pm 0.03$ Å, $b = 13.10 \pm 0.02$ Å, $c = 7.55 \pm 0.01$ Å, $\beta = 112.0° \pm 0.2°$. After soaking in water to convert to the laumontite form, the (100) lattice spacing of the same crystal increased from 13.68 to 13.86 Å and the (010) from 13.10 to 13.17 Å, all ±0.01 to 0.02. There are corresponding changes in the intercleavage angle $(110) \wedge (1\bar{1}0)$. Space group $C2$ or Cm. 48 oxygen atoms per unit cell. Atomic ratios are calculated for numerous analyses including two new ones. It is shown that replacement of calcium by alkalies is both of the plagioclase and of the zeolite type. The composition of laumontite can be expressed by the formula:

$$Ca_x(Na, K)_yAl_{2x+y}Si_{24-(2x+y)}O_{48} \cdot 16\, H_2O$$

where

$$x + y/2 \text{ does not exceed } 4$$

and

$$x + y \text{ is not less than } 4.$$

INTRODUCTION

The calcium-rich zeolite, laumontite, was first found by Gillet Laumont at Huelgoat in Brittany in 1785. It has long excited interest on account of the extreme ease with which it loses water, often crumbling to a powder in the process. On this account some early descriptions referred to it as "efflorescent zeolite." The partially dehydrated form is known variously as leonhardite, β-leonhardite and caporcianite and has remarkably distinctive optical properties. The typical mode of occurrence of laumontite is as rather small and stout prismatic crystals in veins and cavities in crystalline rocks ranging from serpentines and gabbros to granites and schists, but it has rarely been reported in large amount.

During an investigation of the geology of part of the Taringatura Survey District, Southland, New Zealand (Coombs, 1950), laumontite was found to occur in a manner and on a scale which does not appear to have been recorded hitherto. It is one of the most important alteration products in the lower part of a thick series (nearly 30,000 feet) of Triassic tuffs, graywackes, arkoses and siltstones, and many bedded masses are found to consist largely of the mineral. In the first part of the present paper, these and related occurrences of laumontite are described and the paragenesis is discussed. Further details of the chemical and mineralogical changes which have taken place in the series will be reported elsewhere. The major part of the paper describes a laboratory study of the mineral group.

The writer wishes to express his thanks to Professor C. E. Tilley for his unfailing interest and encouragement, to Dr. N. F. M. Henry for invaluable criticism and suggestions, and to Mr. K. Rickson who took the photomicrographs and powder photographs and gave technical assistance with the single-crystal *x*-ray work. The writer is indebted to Dr. M. Hey of the British Museum for providing one of the specimens referred to in this paper. Another specimen was collected during field work financed by a Research Grant of the University of New Zealand for which grateful acknowledgment is also made.

Occurrence in Southland, New Zealand

The lower part (North Range beds) of the Triassic succession in the Taringatura district of Southland consists very largely of altered lithic andesitic tuffs, but among these are many bands of originally glassy material, derived apparently from a slightly more acid magma than the rest. Some of these beds are only a few inches or a few feet thick, but one group, 450 feet thick, and traceable along the outcrop for many miles, consists almost entirely of water-sorted crystal-vitric tuffs. Nowhere in these rocks has glass been found to remain. Sometimes it is replaced by heulandite, but much more commonly by laumontite, and as a result numerous beds have a rather earthy appearance and a whitish or pale buff color. They are estimated to contain 30–80% laumontite. In thin section, groups of adjacent glass shards are seen to have been replaced by single laumontite crystals which together form an aggregate of interlocking grains 0.5–3 mm. across (Fig. 1). Cleavage faces are noticeable on freshly broken surfaces, but crystal outlines are rarely developed.

Plagioclase fragments in the laumontite rocks are invariably albitized (composition An_{0-4}) and are often unattacked by the zeolite. Occasionally in the North Range beds, and very characteristically in graywackes from the near-by Roe Burn beds of probable late Palaeozoic age, albitized plagioclase may be partly or completely pseudomorphed by laumontite which spreads most readily along the (010) cleavage and twinning planes of the feldspar and thus sometimes gives an effect simulating twinning. The same type of alteration occurs in some Jurassic feldspathic sandstones from the Hokonui Hills to the south-east of Taringatura. In at least some of these cases it may be deduced from relict "islands" of little-altered material that the plagioclase originally had a composition in the range of acid labradorite to acid andesine.

In a similar fashion Hutton (1949) found laumontite to be an important product of the break-down of lime-bearing plagioclase in graywackes of the Otama area of Southland. He attributed this to very low grade metamorphism. The Otama graywackes are part of a belt of almost unmetamorphosed late Palaeozoic rocks which separates the south flank of the Otago schists (Turner, 1938) from the Mesozoic sediments described above. The present writer has found that the mineral occurs abundantly along joint planes and shatter zones, replacing feldspar and as pools in the groundmass both in various igneous bodies and in the graywackes at many localities in this belt, and here also residual plagioclase is albitized in its presence. A crush-zone in albitic meta-gabbro $1\frac{1}{4}$ miles 15° E of north from the Otama Hall may be taken as typical.

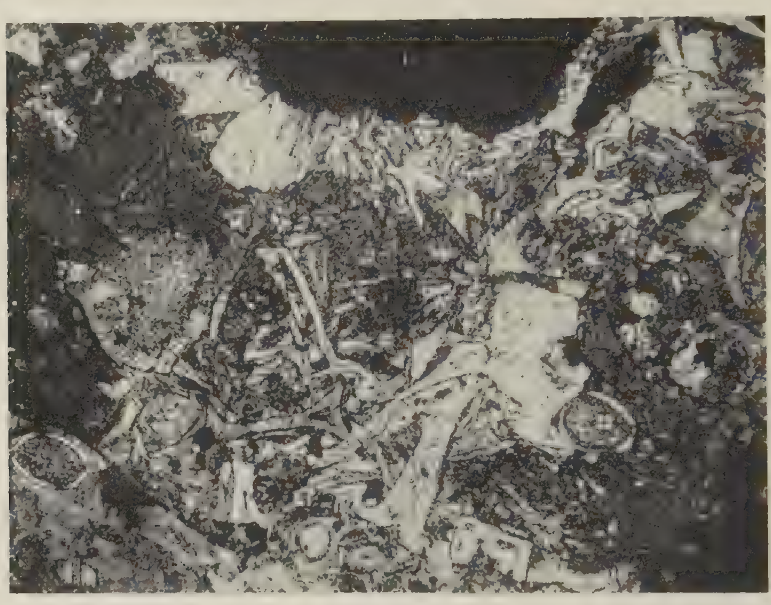

Fig. 1. Laumontitized tuff, no. 8795, North Range, Taringatura Survey District, Southland, New Zealand. A single crystal of laumontite (illuminated) extends right across the field of view, and incorporates many originally glassy ash fragments. These are delineated by dark chloritic films. The shaded region at the lower left and dark regions at the upper left and lower right of the field, represent similar laumontite crystals in near-extinction. Two fragments of twinned plagioclase are also visible. Crossed nicols. ×60.

A sheet of pulverized and slickensided rock several inches thick has been almost completely replaced by laumontite (analysis no. 1, Table III) associated with a little prehnite and chloritic matter and containing broken fragments of augite, albitized feldspar and iron ore from the country rock. Cleavages and cross fractures in these minerals are penetrated by the laumontite.

Hutton (1944) has also described leonhardite replacing andesine in a porphyrite from Devon Well, Paritutu Survey District, New Zealand (analysis no. 12, Table III), and Petrov (1933) has described small apophyses consisting of an aggregate of laumontite (50%), opal, chlorite and zeolitized feldspar given off from a thin sill injected into bedded tuffs in the neighbourhood of Tiflis. It is also interesting to note that Park (1946) found laumontite to be locally abundant in the spilites and associated rocks of the Olympic Peninsula, Washington.

Origin

It is significant that in the thick Triassic section of Taringatura, laumontite is rare or absent in the upper members in which plagioclase is generally unaltered and other mineralogical adjustments are slight. Towards the base of the series detrital plagioclase becomes progressively more commonly albitized, laumontite becomes widespread and other secondary minerals such as pumpellyite and prehnite appear. Laumontite, pumpellyite, calcite and sericite may all occur as inclusions in the albitized plagioclase, or the plagioclase may be entirely replaced by laumontite. In such cases laumontite appears to be a degradation product of lime-bearing plagioclase under incipiently metamorphic conditions (cf. Hutton, 1949). Sometimes the lime and alumina released during albitization of plagioclase are completely removed from the crystal and may contribute to the crystallization of laumontite in joint planes and crush zones as at Otama, and interstitially in porous beds. Under other conditions, perhaps at a slightly higher temperature, the formation is favoured of such minerals as prehnite, pumpellyite and epidote. In the laumontitized tuffs of the North Range, Taringatura, only a part of the lime and alumina were provided by the original glass and the andesine phenocrysts it contained. There is evidence that heulandite, and locally analcime, may have replaced the glass during diagenesis and before laumontitization, but these minerals also are relatively deficient in lime and, in the case of heulandite, in alumina. The lithic tuffs and tuffaceous graywackes with which the laumontite rocks are interbedded have been fairly uniformly albitized and lost appreciable amounts of lime in the process. It appears that interstitial solutions have carried some of this lime to the beds of altering glassy tuff where it has been "fixed" as laumontite.

OPTICAL OBSERVATIONS ON THE LAUMONTITE-LEONHARDITE RELATIONSHIP

It has long been known that on exposure to the atmosphere, or on gentle heating, laumontite loses approximately one eighth of its water to form the sometimes powdery variety known variously as leonhardite, β-leonhardite or caporcianite (e.g. see Des Cloizeaux, 1862, p. 405; Walker and Parsons, 1922; Pagliani, 1948). Simultaneously the refractive indices drop, the extinction angle increases markedly and the optic axial angle changes. In most cases it decreases, but in one (no. 1, Table I) it appears to increase slightly. The ready reversibility of these changes does not appear to have been recorded. When crushed grains of leonhardite are placed in a drop of water between crossed nicols, a zone with the laumontite extinction angle is seen to form quickly at the broken ends of the grains and at any transverse cracks or cleavages (Fig. 2). The boundary between the two zones may be quite sharply defined. It migrates inwards, mainly in the direction parallel to the *c* axis, until after a period which in some specimens may be as brief as an hour or two, the whole grain has assumed the optic orientation of laumontite. Measurements of the optic axial angle and refractive indices show that these properties also return to values characteristic of fully saturated laumontite.

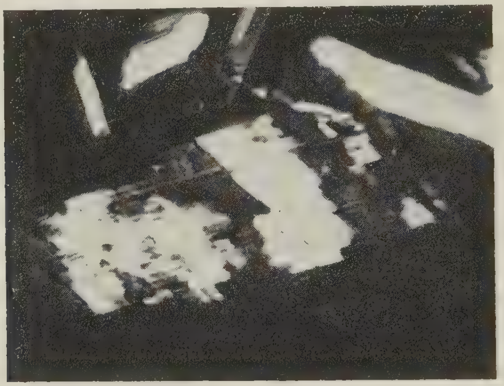

FIG. 2. Cleavage fragment of leonhardite (no. 192, Hungary) after immersion in water for two hours. Regions of rehydrated laumontite at the ends and in transverse fractures are in extinction. Residual leonhardite with its much larger extinction angle is still brightly illuminated. Crossed nicols. Length of grain = 0.2 mm.

In some cases the formation of a leonhardite-type form from powdered laumontite may be watched microscopically in dry air, or more conveniently by immersion in a mild dehydrating agent such as glycerol. Thin sections heated in the usual way during preparation invariably show leonhardite optics. To make accurate measurements of optical properties of leonhardite it was found necessary to use very small cleavage fragments as larger grains frequently failed to extinguish properly, apparently due to distortion and to the superposition of regions of different hydration states. It was noticed that in each batch of crystals studied, the optic axial angle was distinctly variable. In general the maximum extinction angle in the prism zone is neither the angle $\gamma \wedge c$ measured on (010), nor is it the angle often measured on (110) cleavage flakes, as can be shown both by the Biot-Fresnel construction and experimentally on the Universal Stage or stage goniometer. Recorded observations on fully hydrated laumontite indicate that it always has slow elongation, but it may be pointed out that in typical leonhardite the angle $\gamma' \wedge c$ measured in the prism zone increases from a value of 30°–35° measured on (010) to 90° measured on (100). In the latter case the grain has fast elongation (Fig. 3). The leonhardite extinction angle of the Taringatura mineral appears to be unusually low.

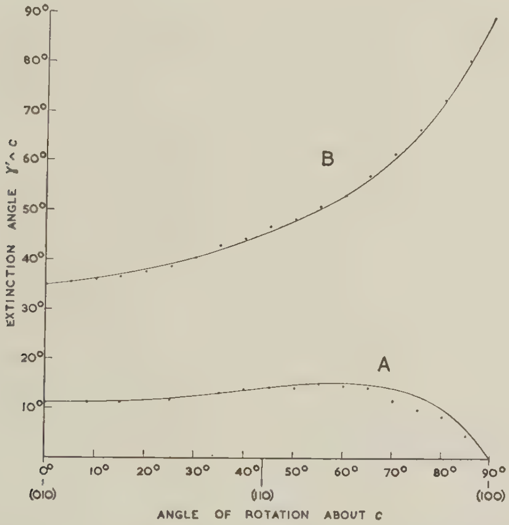

FIG. 3. Extinction angles $\gamma' \wedge c$ in the prism zone of a crystal of laumontite (A), and of the corresponding leonhardite (B). B.M. 67213, Felsö Certes, Transylvania. *Points* refer to angles measured with the help of the one-circle stage goniometer and the *full line* shows the variation as deduced from the Biot-Fresnel construction.

Typical data follow (Table 1):

TABLE I. OPTICAL PROPERTIES OF LAUMONTITES AND THE CORRESPONDING LEONHARDITES

		1	2	3	4
Laumontite	$\alpha=$	1.510±.002	1.514±.002	1.509±.002	1.514±.002
	$\beta=$	1.518±.002	1.522±.002	1.518±.002	1.522±.002
	$\gamma=$	1.522±.002	1.524±.002	1.521±.002	1.525±.002
	$(-)2V=$	39°±5°	33°±5°	41°±3°	47°±3°
	$\gamma\wedge c=$	10°±2°	8°±2°	9°±2°	11°±2°
	$\gamma'\wedge c$ on (110)=	13°±2°	11°±2°	11°±2°	14°±2°
Leonhardite modification	$\alpha=$	1.505±.002	1.507±.002	1.502±.002	1.507±.002
	$\beta=$	1.514±.002	1.516±.002	1.512±.002	1.516±.002
	$\gamma=$	1.517±.002	1.518±.002	1.514±.002	1.518±.002
	$(-)2V=$	44°±3°	26°±4°	36°±4°	38°±5°
	$\gamma\wedge c=$	33°±2°	32°±2°	8—19°	35°±2°
	$\gamma'\wedge c$ on (110)=	39°±2°	40°±2°	11−24°	47°±2°

Marked dispersion $r<v$ in all cases.

β is parallel to b, γ lies in the acute angle β.

1. Crush zone in meta-gabbro, Otama, Southland, New Zealand. Analysis no. 1, Table III.
2. "Laumontite on tuffa, Hungary, No. 192." Mineralogical Museum, Cambridge. The Museum specimen is leonhardite and the laumontite modification was derived from it by soaking in water. Analysis no. 2, Table III.
3. Laumontite from laumontitized vitric tuff, no. 8784, North Range, Taringatura Survey District, Southland, New Zealand. Another specimen from the same locality gave $\alpha=1.506\pm.003$ for the laumontite form and $\alpha=1.502\pm.003$ for the corresponding leonhardite form. Both of these Taringatura specimens were peculiarly resistant to the change and the low extinction angle of their "leonhardite" modification is unusual.
4. Felsö Certes, Translyvania. B.M. 67213. The specimen has been kept continuously over water in the British Museum, but rapidly changes to the leonhardite form on exposure.

Pagliani (1948) considers from dehydration experiments and x-ray powder photographs that no essential change in crystal structure occurs when laumontite loses water to form leonhardite. The reversibility of the changes in optical properties tends to support this, although the apparent suddenness of the transition requires explanation. Pagliani reports that natural leonhardite and laumontite partially dehydrated at 70° C. both gave lines identical in position and relative intensity with those of fresh laumontite. This result is in conflict with observations on the laumontites in Table I as will be shown later. After an initial drop during conversion to leonhardite, both refractive indices and specific gravity were found by Pagliani to remain fairly constant for a while and then to increase as the temperature of heating was raised progressively to 850° C. This is attributed by Pagliani to lattice shrinkage.

The general term "laumontite" is used in this paper except where it is wished to stress the water-poor nature and distinctive properties of a particular specimen. This procedure is normally advisable for records of field occurrences, as in some cases the variety collected from a particular outcrop may vary with the weather.

Gilbert (1951) in a short abstract has just recorded observations very similar to those of the present writer, based on laumontite occurring as cement in a sandstone from Anchor Bay, Mendocino County, California. He notes the ease of rehydration of leonhardite and records the accompanying changes in refractive indices and 2V as follows: fully hydrated laumontite $\alpha=1.515$, $\gamma=1.525$, $(-)2V=45°\pm5°$, $\gamma\wedge c=10°$; variety leonhardite $\alpha=1.506$, $\gamma=1.517$, $(-)2V=30-35°$, $\gamma'\wedge c$ on $(110)=39$–$41°$.

Relation of Optical Properties to Chemical Composition

The effect of dehydration on the refractive indices obscures the effect of alkalies and until more deta are available on material of carefully defined hydration condition, the exact relationship will remain obscure. The data in Table III suggest that indices drop with increasing silica and alkali content in the usual way. Of the analyzed leonhardites which have been described optically, the most silica- and alkali-rich, no. 12, has the lowest indices, $\alpha=1.502$, whereas no. 14 with low alkali content has the higher value $\alpha=1.508$. A similar relationship probably holds for laumontite.

X-Ray Study

The Taringatura and Otama laumontites were not found to be suitable for single-crystal *x*-ray investigation. A specimen of leonhardite, no. 192, from Hungary, in the Mineralogical Museum, Cambridge, was therefore used. Optical properties and a chemical analysis are given in columns no. 2 of Tables I and III, respectively. Examination showed that most crystals have been distorted and opened along cleavage planes, presumably during loss of water from laumontite. Single-crystal oscillation and Weissenberg photographs were obtained from a small cleavage needle by giving long exposures. The same crystal was later placed and sealed in a capillary tube filled with water, and after two days was found by optical examination to have changed completely to the laumontite form. Oscillation and Weissenberg photographs were then taken about the *c* axis. The following cell constants were determined:

Leonhardite form	*Laumontite form*
$a = 14.75 \pm 0.03$ Å	$a = 14.90 \pm 0.05$ Å
$b = 13.10 \pm 0.02$	$b = 13.17 \pm 0.02$
$c = 7.55 \pm 0.01$	$c = 7.55 \pm 0.05$
$\beta = 112.0° \pm 0.2°$	$\beta = 111.5° \pm 0.5°$

In the case of leonhardite, a^*, b^* and c^* reciprocal lattice dimensions were determined from high-angle reflections in the zero-layer Weissenberg photographs taken about the b and c axes, and had a reproducibility of better than 1 in 1,000. The photograph taken about b was used for the determination of β with the probable limits of error indicated. Since the determination of a and c from the reciprocal lattice depends on the function sin β, errors in them are correspondingly greater than in a^* and c^*. The most accurate measurements on the laumontite form relate to the a^* and b^* reciprocal lattice dimensions. From these it is found that the (100) lattice spacing increased during the transition from 13.68 to 13.86 Å and the (010) from 13.10 to 13.17 Å, all ±0.01–0.02 Å. The value given above for the a cell edge is affected by the less accurately determined β angle and c is here based on layer-line spacings. The differential nature of the changes in (h00) and (0k0) spacings, produced simply by soaking in water, or conversely by air-drying, is striking and results in changed intercleavage angle and axial ratio. It is accompanied by the changes in optical properties described above and also explains why laumontite crystals fall to pieces along their prismatic cleavages during partial dehydration.

The axial ratio calculated from the x-ray data for the leonhardite modification is $a:b:c = 1.12_6:1:0.57_6$ and that for the laumontite is $a:b:c = 1.13_1:1:0.57_3$. The corresponding calculated intercleavage angles $(110)\wedge(110)$ are 92.5° and 92.9°, respectively. The leonhardite crystal gave poor cleavage reflections on the optical goniometer indicating an angle $(110)\wedge(1\bar{1}0)$ of 92–$92\frac{1}{2}$°. Although apparently based on the same cell orientation, the x-ray figures, especially those for the leonhardite, differ somewhat from the classical data quoted for laumontite by Dana (1892): $a:b:c = 1.1451:1:0.5906$, $\beta = 68°46\frac{1}{4}'$, $(110)\wedge(1\bar{1}0) = 93°44'$. Other published observations vary from a reported intercleavage angle of 96°30′ (Des Cloizeaux, 1862), which seems too high, to 93°13′ for the same modification (Reichert, 1924). The present study does not rule out the possibility of a modification with such figures, but mere prolonging of the immersion in water is unlikely to produce much further change, as the powder pattern of laumontite no. 192, produced from leonhardite by soaking in water for a few days, is indistinguishable from that of laumontite from Felsö Certes, Transylvania, B.M. 67213 (no. 4, Table I) which has always been kept over water at the British Museum. This specimen was provided through the courtesy of Dr. M. Hey and has not been out of water since it left the Museum about a year before the powder photos were taken.

Powders of leonhardite 192 and of leonhardite produced by air-drying B.M. 67213 were rolled into thin rods with stiff gum tragacanth solution in the usual way for powder photos and allowed to dry. The resulting patterns were identical, but easily distinguished from those of the laumontite form of both minerals when taken in sealed capillary tubes filled with water. Data are given in Table II for specimen 192 after three modes of treatment: (*a*) leonhardite air-dried, (*b*) leonhardite sealed into a capillary tube after drying for three days over silica gel, and (*c*) laumontite produced by soaking in water for several days and sealed into a capillary tube filled with water. After correction for absorption, no significant differences are found between the first two. There is no difficulty in distinguishing the leonhardite and laumontite patterns side by side, but as a quick distinction the position of the two strong lines near 1.63 Å may be suggested. In leonhardite these are close together at approximately 1.623 and 1.635 Å, whereas in laumontite they are noticeably farther apart at 1.627 and 1.646 Å.

The analyzed Otama laumontite 979, air-dried, gave a predominantly laumontite-type pattern, but rather weak though distinctive leonhardite lines are present as well. It is significant that both types of lines should be present rather than continuous shading which would be expected for a gradual transition. This accords with the optical examination in which each grain of laumontite was seen to be coated with a zone having leonhardite optics. The Taringatura laumontite no. 8784, air-dried, gave a purely laumontite type of pattern. It is thus seen that of the four specimens examined by *x*-rays, the two with the lowest refractive indices, and in one case with proved relatively high alkali content, are relatively stable under normal atmospheric conditions as the laumontite modification, whereas the two specimens with higher indices and lower alkali content quickly change to leonhardite on exposure.

On the basis of the axial elements given above, all reflections of the type (hkl) are extinguished when $(h+k)=2n+1$. There are no other systematic extinctions. The cell is therefore *C*-face centred in both modifications. Comparison of the Weissenberg photographs however, shows significant intensity changes in various reflections. Laumontite has usually been assumed to belong to the monoclinic holosymmetric class, $2/m$. Crystals of laumontite and leonhardite from three localities gave a negative result when tested with the Giebe and Scheibe tester for piezo-electric effect, but grains adhered firmly to aluminum foil when immersed in liquid air and removed again, thus indicating a strong pyro-

Table II. Powder Data for Leonhardite and Laumontite, (Specimen No. 192, Hungary)

(Camera 19 cm. diameter, filtered Cu-Kα radiation. $\lambda=1.542$)

Indices	Leonhardite, air-dried		Leonhardite in sealed tube after drying over silica gel		Laumontite in sealed tube with water	
	I/I_1	d in Å	I/I_1	*d in Å	I/I_1	*d in Å
200	6	6.88	6	6.88	6	6.97
$\bar{2}01$	2	6.21	2	6.21	1	6.16
111	2	5.07	2	5.07	1	5.14
220	1	4.75	1	4.75	2	4.77
$\bar{2}21$	3	4.51	3	4.51	1	4.50
130, 201	10	4.18	10	4.18	10	4.18
$\bar{1}31$	<1	3.77	<1	3.75	<1	3.76
$\bar{4}01$	4	3.67	3	3.67	4	3.67
221, 002	10	3.52	10	3.52	6	3.53
400, 131	<1	3.42	1	3.42	1	3.45
$\bar{3}12$	1	3.36	1	3.37	2	3.35
040	3	3.28	3	3.28	3	3.29
$\bar{3}31$ (311, $\bar{4}21$)	2	3.21	2	3.21	3	3.21
330	1	3.16	<1	3.15	1	3.19
$\bar{4}02$	<1	3.09	1	3.10	4	3.08
420, 112	4	3.04	4	3.04		
240 (041)	<1	2.95	1	2.93	<1	2.97
$\bar{5}11$ ($\bar{2}41$)	3	2.88	3	2.88	3	2.89
	2	2.80	2	2.80	2	2.78
	<1	2.73	<1	2.73	3	2.61
	<1	2.64			1	2.60
	3	2.58	3	2.58	<1	2.51
	2	2.52	2	2.53	4	2.45
	1	2.46	1	2.47	2	2.383
	4	2.440	3	2.440	<1	2.347
	<1	2.394	<1	2.391	1	2.287
	2	2.361	2	2.360	1	2.212
	1	2.272	1	2.273	2	2.192
	2	2.216	2	2.218	1	2.180
	1	2.183	1	2.179	1	2.156
	3	2.155	3	2.153	<1	2.115
	1	2.090	1	2.090	<1	2.042
	<1	2.059	<1	2.048	1	2.023
	<1	2.041			<1	1.996
	1	1.994	1	1.997	2	1.968
	2	1.961	2	1.961	<1	1.932
	<1	1.910	<1	1.909	<1	1.908
	<1	1.888	<1	1.886	3	1.864
	1	1.869	2	1.871	<1	1.836
	1	1.852	1	1.850	1	1.785
	<1	1.826	<1	1.828	<1	1.766
	<1	1.796	1	1.798	<1	1.745
	1	1.762	2	1.761	1	1.724
	<1	1.733	<1	1.733	<1	1.688
	1	1.706	1	1.706	<1	1.667
	<1	1.677	<1	1.680	3	1.646

TABLE II (*Continued*)

Indices	Leonhardite, air-dried		Leonhardite in sealed tube after drying over silica gel		Laumontite in sealed tube with water	
	I/I_1	d in Å	I/I_1	*d in Å	I/I_1	*d in Å
	2	1.635	2	1.635	3	1.627
	2	1.623	2	1.623	1	1.602
	<1	1.596	<1	1.598	1	1.586
	1	1.566	1	1.566	2	1.582
	<1	1.544	<1	1.544	<1	1.557
	2	1.523	2	1.521	4	1.535
	<1	1.497			<1	1.519
	<1	1.490	1	1.491	<1	1.502
	1	1.475	1	1.473	1	1.488
	1	1.445			<1	1.477
	2	1.437	2	1.440	2	1.451
	<1	1.423	<1	1.424	<1	1.428
	1	1.404	1	1.406	<1	1.413
	<1	1.387	<1	1.386	1	1.392
	<1	1.375	<1	1.373	1	1.375
	1	1.367	1	1.366	<1	1.359
			<1	1.350	2	1.347
	1	1.342	1	1.342	3	1.341
	1	1.329	1	1.328	2	1.316
	<1	1.315	<1	1.316	2	1.312
	1	1.305	1	1.305	<1	1.296
	<1	1.293	<1	1.293	2	1.278
	<1	1.279	<1	1.278	1	1.266
	2	1.265	2	1.264	<1	1.251
	1	1.256	1	1.256	2	1.236
	<1	1.245	<1	1.246	2	1.209
	1	1.230	1	1.231	<1	1.187
	1	1.191	1	1.190	1	1.177
	1	1.163	2	1.164	<1	1.167
	1	1.151	1	1.150	<1	1.156
	<1	1.132	<1	1.132	<1	1.145
	<1	1.119	<1	1.119	<1	1.108
	<1	1.088	<1	1.087	<1	1.101
	<1	1.046	1	1.046	1	1.092
	<1	1.024	1	1.024	<1	1.052
	<1	.984	<1	.984	<1	1.044
	<1	.975	<1	.975	<1	1.037
			<1	.967	<1	1.034
			<1	.958	<1	1.025
	<1	.952	1	.952	<1	.997
			<1	.942	<1	.989
			<1	.934	<1	.958

* Owing to absorption caused by the glass capillary tubes and the rather thick columns of powder enclosed in them, lines with low and moderate values of θ were displaced somewhat. The apparent spacings were corrected empirically on the basis of observed displacement of lines for the air-dried material when placed in a similar capillary tube.

electric effect. Assuming no phase change in the temperature interval involved, it may be concluded that the structure lacks a centre of symmetry and the space group is either *C*2 or *Cm*.

It may be noted that Fersman (1908) attempted a distinction based partly on physical grounds between "primary" or α-leonhardite with high alkali content and no (010) cleavage and "secondary" or β-leonhardite formed by loss of water from laumontite and retaining the supposedly good (010) cleavage of the latter. These distinctions appear to be of doubtful validity. Gilbert (1951) did not find the (010) cleavage in his material, and no (010) cleavage is visible in the specimens described by the present writer. Another point of possible structural interest is the observation of Murata (1943) that laumontite is an exception to the general rule for silicates with a three-dimensional network that the ratio Al:Si must be greater than 2:3 for gelatinization with acids to occur.

CHEMICAL COMPOSITION

The chemical analysis, specific gravity and cell size for leonhardite 192 (no. 2, Table III) lead to the figure 48.3 oxygen atoms per unit cell, and assuming similar cell sizes for the other analyzed laumontites it may be shown that they also lead to figures approximating to 48 oxygen per unit cell.

Variants of the simple formula $CaAl_2Si_4O_{12}\cdot 4H_2O$ have long been quoted for laumontite, but the presence of alkalies has often been overlooked. Winchell in 1925 stressed the importance of isomorphic substitution in laumontite and other zeolites, but considered that it is confined to the mutual interchange of (NaSi) and (CaAl) as in plagioclase. On the basis of an arbitrarily assumed 80 oxygen per unit cell, he proposed the formula

$$(Na, Ca)_2Ca_5Al_{12}(Al, Si)_2Si_{26}O_{80}\cdot 25H_2O.$$

Hey (1930, 1932) has shown for various zeolites that in addition to the above possibility, pairs of alkali atoms may proxy for Ca without affecting the Si:Al ratio. In 1935 Rossoni suggested for laumontite the formula $(Ca,K_2,Na_2)_2Al_4(SiO_3)_8\cdot 8H_2O$, but unfortunately the analysis he published was made on very impure material and does not accord with fundamental zeolite requirements. As early as 1908, Fersman had proposed a similar formula with one molecule less water for "α-leonhardite."

To test the above possibilities, atomic ratios have been calculated for numerous analyses. An examination of published analyses of laumontite shows that wherever alkalies have been determined, they are present in appreciable amount. Analyses which contain no statement of alkali content are therefore not included in the accompanying Table III. As some of the many analyses which do not include alkali determinations were probably made on material which was in fact alkali-poor, the overall picture set out in the Table may be distorted in this respect. Hey (1932, p. 57) showed that for a first class zeolite analysis $(Al+Si)=40\pm0.20$ as calculated for 80 oxygen atoms per unit cell, from which it follows that $(Al+Si)=24\pm0.12$ calculated for 48 oxygens. Furthermore, the summation must be between 99.70 and 100.80. Doelter (1922) listed 53 analyses of laumontite and leonhardite. Table III contains a selection of those taken from Doelter which satisfy the above requirements together with later analyses falling in Hey's classes "A" and "B." Five other analyses quoted in Doelter, and those published by Reichert (1924), Takats (1936) and Niggli, Koenigsberger and Parker (1940), although not included in Table III, are also compatible with the requirements here adopted. In calculating the formulas, small amounts of Fe_2O_3, TiO_2 and MgO were neglected except in the case of the Table Mountain analyses (no. 4 and no. 9) as Henderson and Glass (1933) give evidence that the Fe''' therein isomorphously replaces Al within the structure.

Starting from the ideal alkali-free end-member formula $Ca_4Al_8Si_{16}O_{48}\cdot16H_2O$ to which many of the analyses closely approximate, substitution purely of the plagioclase type suggested by Winchell would result in the sum $Ca+Na+K$ remaining constant at 4, while Si would increase and Al decrease by an amount equal to the number of alkali atoms. This condition is approximated by only one analysis, a very old one, no. 6, which like many other analyses is unsupported by optical data. If substitution were purely of the type $Ca=2(Na,K)$, the sum $Ca+[(Na+K)/2]$ should remain at 4, and Si and Al should remain at 16 and 8, respectively. This condition is approached by analyses 1 and 3, although in both of these there is a slight deficiency in Si. Other analyses show the same effects less strongly. The work of Lemberg (1877, 1885) and others indicate that experimental replacement of Ca by alkali metals can readily be achieved in this way, but unfortunately Lemberg did not examine his products optically. Formulae calculated from his earlier analysis of leonhardite from Schemnitz (1877, no. 58) and of the soda-laumontite produced from it (*loc. cit.* no. 58*a*) are as follows:

58. $(Ca_{3.63}Na_{0.18}K_{0.22})Al_{7.78}Si_{16.25}\cdot13.37H_2O$.

$$Ca + Na + K = 4.03; \qquad Ca + \frac{Na + K}{2} = 3.83.$$

58*a*. $(Ca_{1.38}Na_{4.86}K_{0.06})Al_{7.73}Si_{16.29}\cdot13.00H_2O$.

$$Ca + Na + K = 6.30; \qquad Ca + \frac{Na + K}{2} = 3.84.$$

Several analyses show a combination of both types of isomorphic substitution. Hutton (1944) commented on the excess of lime and alkalies

TABLE III. CHEMICAL ANALYSES, OPTICAL PROPERTIES AND FORMULAE OF LAUMONTITE

	1	2	3	4	5	6	7
SiO_2	50.63	52.04	50.94	51.43	52.07	53.67	50.96
TiO_2	0.05	—	—	—	—	—	—
Al_2O_3	22.07	21.46	22.30	21.52	21.30	20.44	21.60
Fe_2O_3	0.73	0.12	0.12	0.94	—	0.59	0.03
MnO	tr.	—	—	—	—	—	—
MgO	0.40	tr.	—	—	—	—	—
CaO	10.72	11.41	7.65	11.88	11.24	9.79	11.27
Na_2O	1.08	0.20	2.06	0.19	0.48	0.59	0.32
K_2O	0.45	0.66	4.01	0.35	0.42	1.25	0.18
H_2O	14.10	13.80	13.42	13.81	14.58	13.52	16.04
	100.23	99.69	100.50	100.12	100.09	99.85	100.40
Sp. Gr.	2.30 ± .02	2.29 ± .01	2.30–2.31	—	—	—	2.283
α	1.505	1.507	—	—	—	—	—
β	1.514	1.516	—	—	—	—	—
γ	1.517	1.518	—	—	—	—	—
$2V_\alpha$	44° ± 3°	26° ± 4°	—	—	—	—	—
$\gamma \wedge c$	33°	32°	—	—	—	—	small
$\gamma' \wedge c$ on (110)	39°	40°	—	35–40°	—	—	—

Atomic formulae on basis of 48 Oxygen atoms

	1	2	3	4	5	6	7
Ca	3.60	3.79	2.55	3.93	3.74	3.23	3.79
Na	0.65	0.12	1.24	0.12	0.28	0.35	0.19
K	0.18	0.26	1.59	0.14	0.17	0.49	0.07
Al	8.17	7.84	8.19	8.07	7.80	7.47	8.00
Si	15.87	16.13	15.87	15.92*	16.17	16.57	16.04
H_2O	14.71	14.23	13.93	14.25	15.08	14.01	16.81
Ca+(Na+K)/2	4.02	3.98	3.97	4.06	3.97	3.65	3.92
Ca+Na+K	4.43	4.17	5.38	4.19	4.19	4.07	4.05
Al+Si	24.04	23.97	24.06	23.99	23.97	24.04	24.04

* Includes 0.22 Fe‴.

† "B"—class analysis.

‡ Includes 0.52 Fe‴.

‖ "Maximum extinction angle."

TABLE III. *Continued.*

	8†	9	10	11†	12	13†	14
iO$_2$	50.64	50.82	51.45	51.36	54.10	48.96	50.24
TiO$_2$	—	—	—	—	0.11	—	—
l$_2$O$_3$	21.86	20.06	22.74	22.55	20.44	22.24	23.64
e$_2$O$_3$	—	2.18	0.20	0.24	1.70	—	—
InO	—	—	—	—	0.05	—	—
lgO	0.74	0.02	—	0.17	0.45	—	—
aO	12.18	12.14	11.70	11.18	8.65	12.32	12.72
a$_2$O	0.42	0.31	0.14	0.12	2.60	0.63	0.35
$_2$O	1.34	0.22		0.28	0.55	0.31	0.15
$_2$O	13.59	14.87	13.77	14.56	11.45	16.41	13.36
	100.77	"99.97"	100.00	100.46	100.10	100.87	100.46
p. Gr.	2.23	—	2.2–2.3	2.281	2.38	2.265	2.241
	1.505	1.504	1.508	1.510	1.502	1.519	1.508
	—	1.514	—	—	1.512	1.525	—
	1.513	1.516	1.524	1.520	1.514	1.527	1.516
V$_\alpha$	—	—	—	—	35–38°	—	—
$\wedge c$	40°	30–36°	—	—	—	10–14°	35–36°
$'\wedge c$ on (110)	—	—	30°	—	40°‖	—	—

Atomic formulae on basis of 48 Oxygen atoms

	8†	9	10	11†	12	13†	14
a	4.05	4.08	3.86	3.71	2.84	4.19	4.18
Ia	0.25	0.19	0.07	0.07	1.54	0.38	0.21
	0.53	0.09		0.11	0.21	0.13	0.06
l	8.02	7.93‡	8.24	8.24	7.39	8.32	8.55
i	15.76	15.95	15.86	15.92	16.60	15.54	15.43
$_2$O	14.09	15.53	14.13	15.04	11.71	17.36	13.66
a+(Na+K)/2	4.44	4.22	3.90	3.80	3.72	4.45	4.32
a+Na+K	4.83	4.36	3.93	3.89	4.59	4.70	4.45
l+Si	23.78	23.88	24.10	24.16	23.99	23.86	23.98

* Includes 0.22 Fe‴.

† "B"—class analysis.

‡ Includes 0.52 Fe‴.

‖ "Maximum extinction angle."

EXPLANATION TO TABLE III

Note: In all cases total water is listed.

1. Laumontite partially dehydrated to leonhardite by exposure. Otama, Southland, New Zealand. The Fe_2O_3 and MgO are due to a little finely intergrown ferruginous matter. Optical properties refer to the leonhardite form (cf. Table I). (D. S. Coombs, anal.)
2. Leonhardite, Hungary, no. 192. Mineralogical Museum, Cambridge. (D. S. Coombs, anal.)
3. "Primary leonhardite," Kurzow'schen, Russia. Fersman (1908).
4. Yellow crystals, Table Mountain, Colorado. Cross and Hillebrand (1885). (W. F. Hillebrand, anal.)
5. White crystals, Table Mountain, Colorado. Cross and Hillebrand (1885). (W. F. Hillebrand, anal.)
6. St. Johns, St. Bartholomew Is., West Indies. Cleve (1870). (Th. Nordström, anal.)
7. Laumontite, Margaretville, Nova Scotia. Walker and Parsons (1922). (E. W. Todd, anal.)
8. Leonhardite, Cascade Mountains, Southern Oregon. McClellan (1926). (E. V. Shannon, anal.)
9. Golden-brown crystals, Table Mountain, Colorado. Henderson and Glass (1933). (E. P. Henderson, anal.)
10. Enoggera, Queensland. Whitehouse (1937). (Queensland Govt. Analyst). Recalculated to exclude 0.36% CO_2 as $CaCO_3$, but including H_2O- which was excluded in Whitehouse's recalculation.
11. Markovice, Bohemia. Kratochvíl (1941).
12. Devon Well, New Plymouth, New Zealand. Hutton (1944). (F. T. Seelye, anal.)
13. Fresh crystals of laumontite, Baveno. Pagliani (1948).
14. Leonhardite powder, Baveno. Pagliani (1948).

over the "theoretical" value in his Devon Well analysis (Table III no. 12). The formula for this could be derived by replacement of 0.61 CaAl by 0.60 NaSi and by further replacement of 0.55 Ca by 1.15 Na+K. The discrepancies are within the limit of analytical error. In such cases $Si>16$, $Ca+Na+K>4$, $Ca+[(Na+K)/2]<4$.

To summarize, introduction of alkalies into laumontite may be both of the plagioclase type in which Na and Si atoms simultaneously proxy for Ca and Al atoms, and of the zeolitic type in which two alkali atoms replace one of Ca. This latter type of base exchange may be carried out experimentally and no doubt can occur in nature if the mineral is exposed to alkaline solutions.

Most analyses appear to have been made on leonhardite or laumontite partially dehydrated by exposure. Assuming 16 H_2O for 48 oxygen atoms in the structure of fully hydrated laumontite, we may express its composition by the formula

$$Ca_x(Na, K)_yAl_{2x+y}Si_{24-(2x+y)}O_{48}\cdot 16H_2O,$$

where $x+y/2$ does not exceed 4 and $x+y$ is not less than 4 or less precisely by the simple formula quoted above.

In conclusion it may be recalled that Henderson and Glass (1933) have indicated that Fe''' may proxy for Al to yield yellow and golden-brown crystals, and varieties rich in Be and V have been reported by the Italian workers Gallitelli (1928), Fagnani (1948) and Pagliani (1948, p. 179); and by Fersman (1922), respectively. Spectrographic analyses of two laumontite-rich rocks from Taringatura, kindly carried out by Dr. S. R. Nockolds, did not reveal significant quantities of either of these elements and showed that the content of Ba, Sr and Rb in the laumontite is very much less than in heulandite and adularia from the same area.

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DEVELOPMENT AND GROWTH OF CORDIERITE IN PARA-LAVAS*

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ABSTRACT

Several specimens of para-lavas from Bokaro coalfield formed by fusion and recrystallization of sedimentary rocks due to the burning of underlying coal seams, show numerous crystals of cordierite. The size, shape, development and growth of these crystals are here described and four general types have been distinguished: (*a*) small symmetrical hexagonal grains, (*b*) clusters of spiral shaped grains, (*c*) linked parallel clusters of hexagonal grains or rings, and (*d*) large, imperfect grains with tentacles or multiple terminations.

The conditions and rate of growth, responsible for the formation of these four general types and influencing the size, shape, idiomorphism, perfection, symmetry and pattern of twinning of these crystals are discussed.

The preferred and easy growth towards the solid angles and edges and along the prism faces of the pseudohexagonal prism, and the sluggish growth towards the prism face in rapidly grown cordierite crystals, are explained as being due to the degree of saturation of the atoms or molecules at these spots which afford the greatest or least total co-ordination, and also probably due to the development of lineages in earlier stages. The peculiarities of the atomic structure may influence this preferred growth by controlling the location, number and angular relations of these sites of easy and quick growth.

It is shown that slow, symmetrical mode of growth favors the formation of small star shaped twins and symmetrical concentric twin patterns, while rapid growth in preferred directions yields an irregular concentric twin pattern.

INTRODUCTION

In 1916, L. L. Fermor collected from the Bokaro coalfield several specimens of fused shale and sandstone. These and the rocks from a coalfield in Korea (Madhya Pradesh) originally described as the Chirimiri volcanic series, he termed para-lavas on the analogy of para-gneiss, para-schist, etc. They are known to be produced by the fusion of sedimentary rocks by the burning of coal seams (13). Crystals of cordierite are very common in some of these specimens and it is the purpose of this paper to describe these crystals with special reference to their size, shape, growth and development.

Rocks similar to these and formed by fusion and subsequent recrystallization of sedimentary and even metamorphic rocks may be produced by the agency of heat, either artificial or derived from the burning of coal or oil, magmatic intrusions or lavas. When the heat is of magmatic origin the resulting rock is usually termed a buchite (or basalt-jasper), which is essentially composed of glass and one or more characteristic crystalline phases. Mutual transfer of material between the sedimentary and igneous reactants is often recognized (28).

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Numerous references to these fused and recrystallized rocks are found in literature. The earliest papers are in German by Zirkel (32), Mohl (22), Hussak (21) and Prohaska (24) to name a few. Harker (19) and Flett (15) recognized buchites formed by the fusion of sandstones and phyllites, respectively, near the contacts of igneous intrusions. Thomas (28) and more recently Tomkeieff (29) have described buchites formed by fusion of aluminous xenoliths in a thoelitic magma and of sandstone by the intrusion of a dolerite plug.

Indian examples of buchites and vitrophyric rocks, formed in sedimentary strata by the burning of underlying coal seams at the outcrops, have been described by Chatterjee and Ray (10) and Sharma, Misra and Bhatnagar (26). Both papers give a general petrographic description of these rocks and their mode and temperature of formation. Rocks produced in a similar way have also been recorded by Bastin (1), Rogers (25) and Brady and Greig (2). Fused spent shale from a retort with similar mineral and textural characters as the buchites have been studied by Phemister (23).

Cordierite forms an important and persistent crystalline phase in most of the buchitic rocks described, but so far no attempt seems to have been made to study in detail the stages of growth of this mineral.

A detailed petrographic account of the rock collection under study does not appear to have been published and a mere mention of the minerals recognized in these rocks by Hayden (20) and a short description of the pleochroic iron cordierite by Fermor (14), were the only references located.

PETROGRAPHY

Three of the specimens from Fermor's collection, 23/855 Cordierite-pyroxene vitrophyre, 23/951 Cordierite vitrophyre and 23/952 Cordierite-labradorite vitrophyre, showed a better development of cordierite and over two dozen sections cut from these were studied in detail. Half the number of the thin sections were also examined with the help of a Fedorov stage.

Of the three specimens chosen, 23/951 and 952 are dark grey to black, fine grained and tough rocks resembling basalts. Small vesicles coated with some yellowish material are sometimes found on closer examination. The third is also quite similar to these but shows a vesicular structure more prominently. Blocks of unfused shaly matter are seen enclosed in the molten material (2) which has a rough reniform appearance on the surface.

Under the microscope they show a vitrophyric texture with dark brownish grey glass in which cordierite, labradorite, enstatite and magnetite have been recognized occurring as different assemblages in each specimen. Some corundum (?) and sillimanite have also been observed in other specimens from the same collection.

The cordierite generally occurs as pseudohexagonal prisms which vary from euhedral to anhedral and irregular shapes. In prismatic sections they are rectangular and show negative elongation. All the grains examined are optically negative and the optic axial angle ranges from 68°–75°. Twinning is almost of universal occurrence and inclusions are sometimes present. The light yellowish brown enstatite is seen to build laths or square prisms showing good prismatic cleavage, and straight extinction. Skeletal crystals and prisms with forked terminations are also observed. Rough rosettes comprising small slender laths of labradorite which are generally built of two or three twinned lamellae are quite abundant in the glass. Skeletal shapes are also fairly common. Magnetite occurs as skeletal, dendritic or microlitic growths and is distributed throughout the groundmass. It is very abundant in specimen 23/855. Large irregular crystals and octahedral grains are also common when it occurs in large proportions. Spherulitic growths are quite common in specimens 23/855 and 952.

The glass varies from a light yellowish brown transparent variety to a dark brownish grey, nearly opaque variety. In some places it is completely isotropic and in others it shows signs of devitrification and carries microlites and spherulites.

The general sequence of crystallization deduced from a study of the inter-relation of the minerals shows that magnetite was perhaps the earliest to start crystallizing followed soon by cordierite. Labradorite probably appeared towards the end of the growth of cordierite. Some little magnetite also started separating at this stage. The pyroxene (enstatite) and corundum(?) are among the last to crystallize.

Description of Cordierite Crystals

The cordierite crystals in these specimens can be roughly divided into four general types depending upon their size, shape, perfection and grouping. It will be seen that some of the types grade into others. A short description of each of these four different types is given below:

I. *Small symmetrical hexagons:*

These have generally perfect hexagonal outlines though, in a few, some of the sides are not fully grown. They are small in size, 0.05 mm. to 0.17 mm. across the base and .09 mm. to 0.25 mm. in length. Usually they are about one and a half times as long as broad and form perfect rectangles in longitudinal sections with a tendency in some to be more equidimensional. These crystals occur usually singly and not in clusters

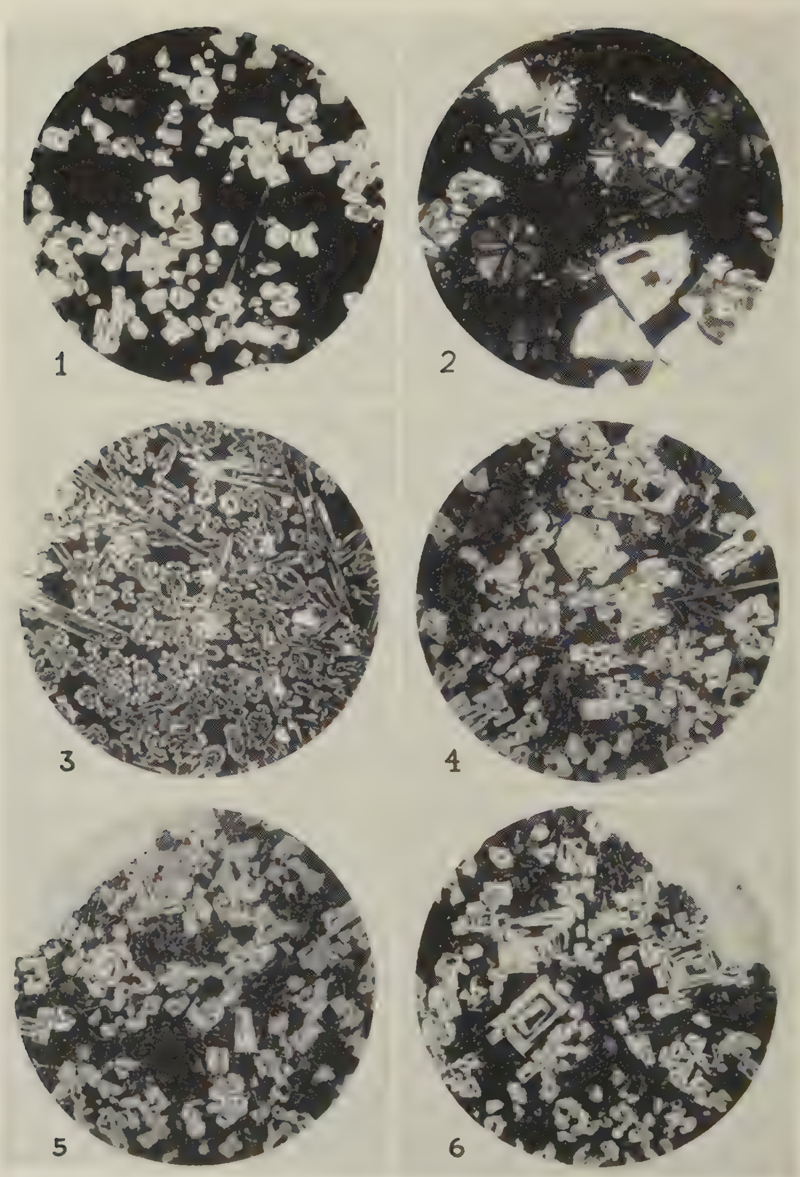


Plate 1. Photomicrographs of cordierite crystals in para-lavas.

Fig. 1. Small symmetrical hexagonal crystals with cavities at the centre embedded in glass. ×10.

Fig. 2. Star shaped radial twinning in small cordierite crystals. Crossed nicols. ×32.

Fig. 3. Crystal clusters and wreaths of types II and III exhibiting early stages of growth. ×10.

Figs. 4 and 5. Rapidly grown crystals of type IV showing the multiple terminations and preferred growth. ×10.

Fig. 6. Prismatic sections showing the preferred growth towards the corners. ×10.

with the individual crystals attached or linked with one another. Voids or glassy inclusions and growth lines are rare but some specks of magnetite are sometimes seen. Radial twinning producing star shaped forms (under crossed nicols) are prevalent and only occasionally does a concentric twin lamella occur. Some of these are pleochroic, colorless to pale mauve. This type is the only one present in specimen No. 23/855 and similar rocks and it is not very common in the others.

Similar haxagonal grains of a slightly larger size measuring 0.15 mm. to 0.24 mm. across in basal sections, are present in specimen 23/952 where large irregular crystals and different types of crystal shapes and clusters are predominant. Radial twinning is occasionally seen in these but a concentric pattern is much more frequent, though in a few cases radiating star-shaped cores are present in the grains showing concentric twinning. These crystals occur in small clusters with overlapping boundaries. Dusty inclusions and hexagonal glassy enclosures at the centre are commonly observed (Fig. 1).

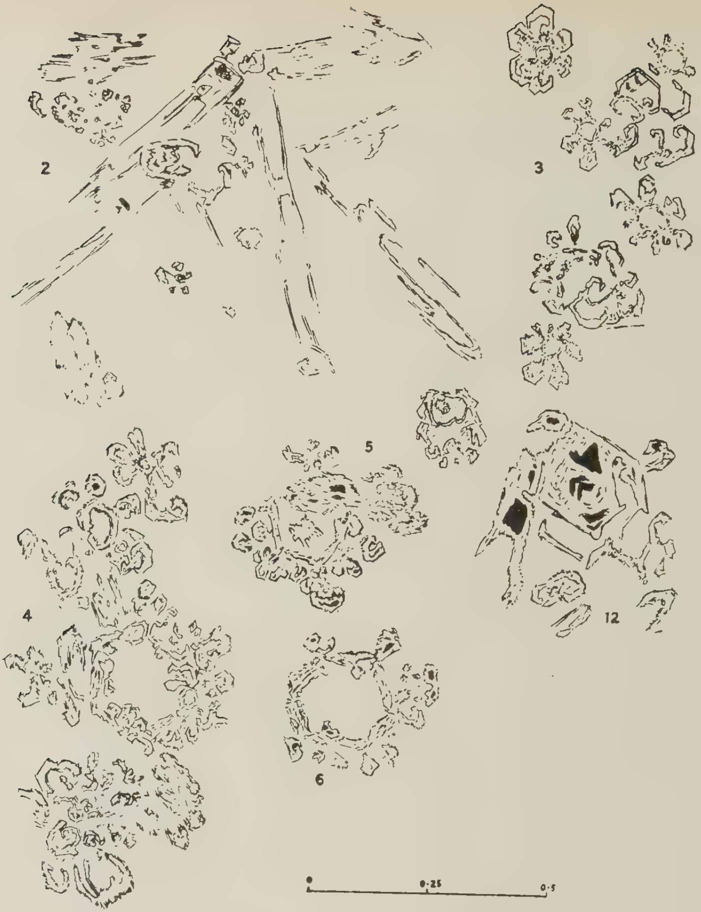
II. *Spiral clusters:*

In specimen 23/951 and to some extent 23/952, the cordierite tends to form hexagonal spirals as viewed in basal sections (Pl. II, Figs. 3, 9). These spirals occur in clusters, overlapping one another when small but when sufficiently big, the individuals might merge together and form a large spiral (Fig. 7), or a partially formed hexagon (Figs. 10, 12). The arms of the spirals have dusty and glassy inclusions either permeating evenly or more commonly concentrated as parallel streaks along their length. The arms often show twinning with the trace of the twin planes usually parallel to the arms or sides. The spiral type is probably an early stage of crystal formation and is closely allied in many respects to the succeeding type.

III. *Linked, parallel clusters of hexagonal rings and grains:*

These generally occur in groups and clusters with fairly well developed hexagonal outlines which are parallel for all individual crystals in the same cluster. The surrounding smaller individuals are grouped around a central one which itself might be a spiral, hexagonal ring or partly formed hexagon, like the satellites. This type of wreath-like arrangement of cordierite grains is very characteristic of specimen 23/951. There is a tendency for the subsidiary individuals to prefer the corners of the central hexagonal framework, though sometimes they also grow along the sides, both inside and outside of the central ring. (Figs. 3–6). These are perhaps the earliest stages of crystal growth, probably contemporaneous with the spiral type.

Twins are not so well developed, but the twin lamellae are often parallel to the sides. Usually the crystals are spirals, skeletals, or rings containing



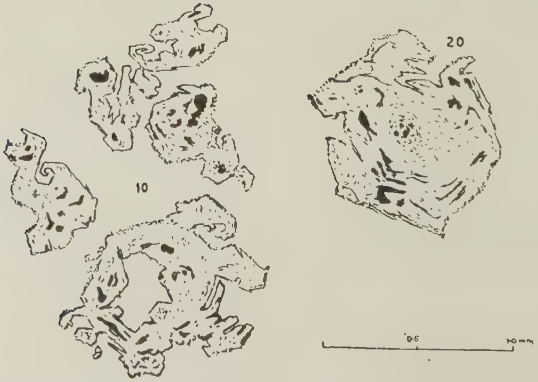
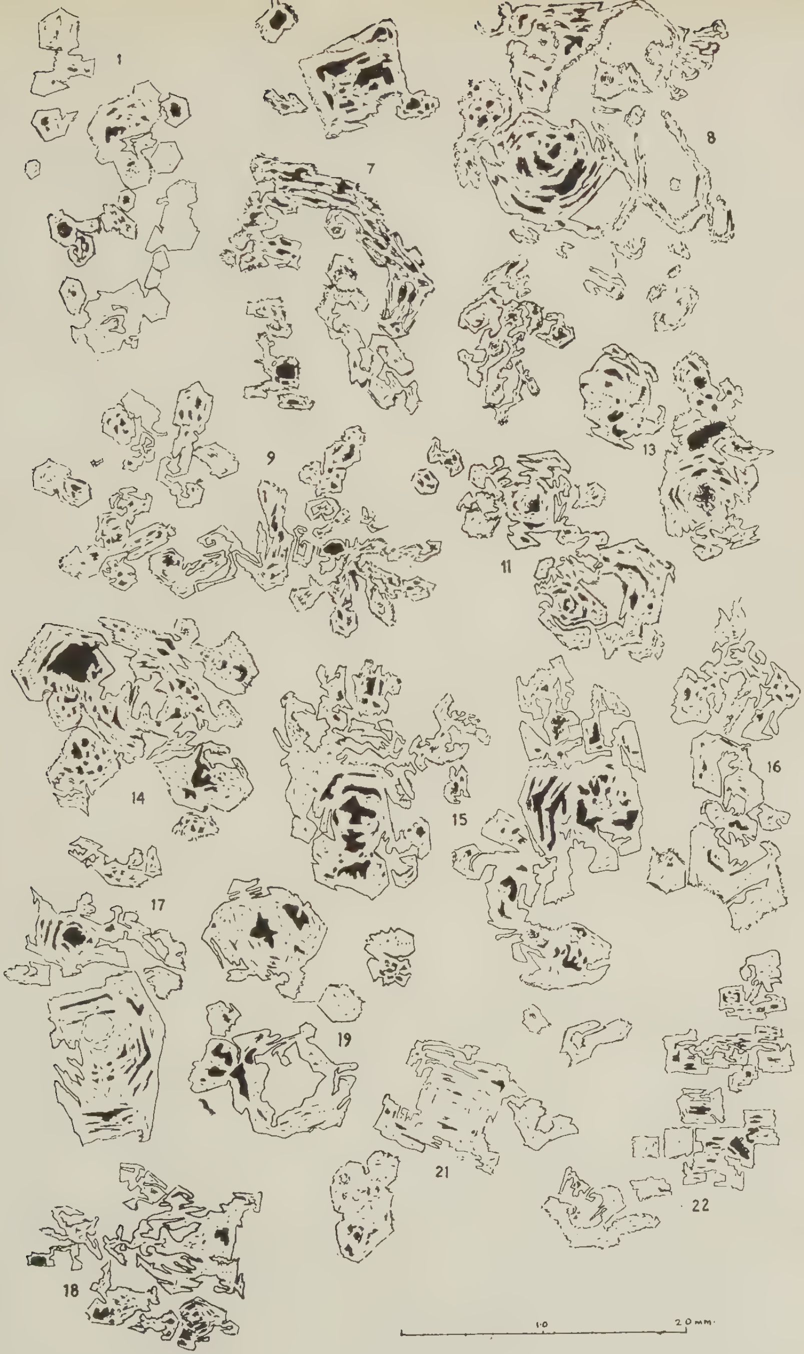


PLATE 2. Camera Lucida drawings of cordierite crystals illustrating the stages of growth and mode of development.

FIG. 1. Small symmetrical hexagonal grains. Type I.

FIGS. 2 to 6. Clusters and wreaths of small crystals in early stages of growth. Note parallelism of boundaries, mode of attachment to central grain, and ring and spiral shaped grains. Types II & III.



FIGS. 7 to 9. Later stages of growth of the crystal clusters producing large spirals or imperfect hexagonal grains.

FIGS. 10 to 20. Rapidly grown imperfect grains showing tentacles or multiple terminations. Note the rapid growth towards the hexagonal corners and the secondary branches parallel to the hexagonal sides. Type IV.

FIGS. 21 & 22. Prismatic sections showing the preferred and rapid growth towards the corners.

inclusions of glass at the nucleus or along growth layers. When the grains are small and euhedral, radial twinning producing stars is occasionally seen.

The outer crystals are attached to the central grain by means of thin channels of minute specks of the same mineral. Sometimes, the channels or arms are seen to be discontinuous or indistinct and in a few cases there are no connecting channels at all. These links connect generally the corners of the crystals but often also the sides of the central frame-work and the corners of the outer individuals. Spirals are commonly seen growing from the central parent with their sides welded together (Figs. 3, 4 and 7).

These linked clusters grow very long parallel to the *c* crystal axis and form bunches or bundles of rod or pencil-like crystals which have many hollows filled with glass along their length (Fig. 2). They have the shape of the letter *H* or of a bobbin, so characteristic of skeletal growth. The boundaries of the grains are rather hazy and indistinct.

An entire wreath or cluster varies in size from .08 mm. to 0.25 mm. in a basal section. The central crystal, when ring shaped, measures .01 mm. to over 0.2 mm. across. Surrounding grains attached to this central one are generally .01 mm. or less to over .05 mm. These are usually smaller if the central framework is large and *vice versa*. The bundles are 0.8 mm. to 2.5 mm. in length.

IV. *Hexagons with tentacles or multiple terminations:*

These are of much later stages of growth where the clusters described above have grown filling the glassy enclosures to form large sized irregular grains measuring .05 mm. to even 1.0 mm. across the basal sections. The larger size is partly due to the numerous branching outgrowths, but different sizes are not uncommon in the same microsection. In this type the arms grow out from the central parent towards the six hexagonal corners but not towards the sides or prism faces. These arms then send out secondary branches parallel to the hexagonal sides and thus try to build a crystal first along the corners and later along the sides from the adjacent corners as is well illustrated in Figs. 8–20. These arms and branches separate out from the parent stalk at angles of 60°. Numerous, fairly big glassy enclosures are present in the central portion of the grain as well as between and within the arms and branches. Their arrangement is, obviously, roughly parallel to the growth layers. These grains with the different branches of growing parts having multiple terminations resemble spread out tentacles.

Sections roughly parallel or slightly inclined to the *c* crystal axis show numerous rectangular prisms of cordierite grouped together in clusters.

In each cluster the long directions of the individual prisms are all roughly parallel thereby showing that they are all parts of a single growing unit. Some of these rectangular prismatic sections show a pronounced growth along the corners and slower and inadequate addition of material along their sides (Fig. 7, 21 and 22). A slender needle of a different mineral is sometimes seen lying in a diagonal direction pointing to the corners of these rectangles.

The prisms vary a great deal in size even within a single thin section. The whole cluster with smaller individual prisms in parallel alignment, measures 0.15 mm. to 2.0 mm. and the smaller individuals 0.17 mm. to 0.7 mm.

All the prismatic sections show traces of twinning planes roughly parallel to the *c* crystal axis (15). In the basal sections the twinning is seen to be mostly distorted and rather complex. Radial, concentric and mixed tendencies (30) are all present. The composition planes are irregular, zigzag and indistinct and the crystal looks like a mass of intricate inter-growth or an aggregate of oddly shaped angular grains fitting as in a jig-saw puzzle. Occasionally there is a small radiating star at the core around which the twinning has developed rather irregularly and indistinctly. When a hexagonal cavity or glassy inclusion is recognizable at the centre, the twinning is more likely to be concentric in pattern reminding one of a spiral or ring shaped parent. Towards the periphery and along the secondary branches from the growing arms, there is a strong tendency for the twin lamellae to lie parallel to the hexagonal sides.

Stages and mode of Development of the Crystals

The earliest forms of crystal formation are the second and third types where skeletal crystals and smaller sizes are common. These are also in clusters, each small grain being attached or linked to another and aligned parallel to one another (Pl. II, Figs. 3–6). They represent the different centres of formation of spontaneous nuclei around which crystal growth starts in an area. It is well known that there is a field of attraction around nuclei and nuclei agglomerates (18). The atomic structure of the earlier nuclei influence and guide the later ones to align themselves in parallel position so as to form a single continuous and homogeneous unit, and this arrangement gives the maximum bonding, cohesion and stability for the later nuclei, especially when they have similar atomic structure. Thus clusters with individuals in parallel alignment are formed.

At this early stage, two modes of growth are possible for the newly formed crystal nuclei. They can grow along their sides, in course of time producing spirals or rings, or they may grow as normal pseudohexagonal prisms adding successive concentric hexagonal layers to the nuclei. In the former case, growth lines, inclusions and irregularities of twinning, shape and size are more common than in the latter. The rings and spirals are very similar since the ring gets formed when the growing arm of a spiral reaches back to its tail but if it overshoots or undershoots to miss the tail, it becomes a spiral awaiting a further opportunity to grow and coalesce with the inner or outer layers eliminating the whorls.

In later stages, the rings, spirals and whorls may grow to quite large sizes with all their irregularities and imperfections, or alternately give rise to a tentacled hexahedron or even to an imperfect pseudohexagonal prism. But the small sized symmetrical hexagons with perfect star shaped radial twins formed by slow, regular growth do not reach large sizes.

These smaller, well developed, six sided crystals are generally confined to specimen No. 23/855 in which no other types are seen. They are however, occasionally met with in specimens 23/951 and 952. The clusters with individual rings and spirals of small dimensions are very characteristic of 23/951 which shows the initial stages of development of the crystals. In 23/952, these clusters grown to slightly larger sizes are observed, but the much larger irregularly grown hexagons (type IV) are much more common. It has not been possible to say whether the small radially twinned perfect hexagons (type I) have grown from these clusters; but it appears very unlikely. They have probably grown from nuclear stages with ordered and uniform-growth in all directions by addition of symmetric layers all round. However, the small crystals with perfect concentric twin patterns appear to have grown from types II and III. On the other hand, it seems quite clear that the crystals of type IV have developed from types II and III.

The size of a crystal depends on two factors, viz. the rate of formation of nuclei and the velocity of growth, and the crystal size equals (31):

$$\text{Constant} \times \sqrt[4]{\text{Velocity of growth/rate of formation of nuclei.}}$$

The well-known curves of Tamman and Miers correlating power of spontaneous crystallization (or nuclei formation) and super-cooling show that the former is maximum at the later labile stage when numerous centres of crystallization develop, than at the earlier metastable stage. This affords the classical explanation of the coarse-grain size of the slowly cooled rocks as compared to the fine-grained nature of the quickly cooled ones. Davey (12) shows how crystallization from a melt is quite analogous to crystallization from a solution; melt becoming synonymous with solution, freezing with precipitation and undercooling with supersaturation. He mentions how Von Weimarn has shown that the size of crystals obtained from pure solution by spontaneous crystallization is a function of the solubility (S), degree of supersaturation (P) and co-efficient of the viscosity of the solution (n) related to the dispersion co-efficient (δ), by the formula $\delta=(P/S)n$. When δ is small the crystallization would be slow and crystals probably perfect, and when it is large, the number of spontaneous nuclei is great and it is very likely that crystals are less perfect.

The perfection and symmetry of a crystal form depends on its rate of growth and it is recognized that the slower the rate of growth, the more perfect a crystal is. Thus, the two controlling conditions of the size and perfection of crystals are the rate of nuclei formation and velocity of growth which in turn depend upon (*a*) the degree and rate of undercooling, (*b*) the viscosity of the melt controlling the rate and ease of diffusion, and (*c*) the molecular concentration or proportion of the crystallizing material in the melt.

It is evident that the para-lavas were formed by the fusion of sedimentary rocks which were cooled relatively rapidly being exposed to atmospheric conditions. Specimen No. 23/855 showing the small, well formed symmetrical crystals of type I has cooled comparatively less rapidly than the others. The total volume percentage of cordierite in this rock is also less in comparison to the other specimens. Both these factors have influenced the formation of relatively few nuclei, and slow rate of growth producing the small and more perfect crystals. Specimen No. 23/951, on the other hand, shows a large quantity of crystals of types II & III which are small skeletal shapes in the form of rings, spirals, etc., building clusters or hexagonal wreaths. It is evident that this specimen, also comparatively fine grained, has cooled rapidly, reaching the labile stage quickly and giving rise to numerous nuclei but the growth was stopped abruptly soon after. In the last specimen, i.e. 23/952, where the crystals are mainly of type IV, the growth was carried on rapidly on account of the concentration of requisite material as indicated by the high volume percentage of cordierite in the rock. During this rapid growth, the crystals developed irregularly and in preferred directions, yielding the large, imperfect crystals with many glassy enclosures and a grotesque and often unrecognizable twin pattern showing wavy and zig-zag twin planes. But growth was perhaps moderate and slower even for these in earlier stages as evidenced by some of the small, more perfect crystals with good twin patterns and few inclusions, occurring separately, or as cores of the bigger imperfect grains.

Imperfections and irregularities in crystals are very normal and common, as remarked by Davey (12). Dendritic shapes and imperfect crystals are the results of rapid growth. When there is a quick shower of the atoms or molecules on a growing crystal, there is not enough time for the impinging atoms or molecules to adjust themselves and fit into the right positions which becomes more and more difficult as it grows to larger sizes as pointed out by Bragg (3); and after a stage growth may be difficult and may even cease on account of the cumulative irregularities and of structural disorder on the rapidly growing surface. Hence, the incoming atoms and molecules place themselves roughly in positions which allow of quick and comparatively easy attachment giving rise to imperfections, irregularities and distortions. But in the case of a crystal growing at a slow and steady pace, it is easier (within limits and up to a stage) for the molecules and atoms to seek out proper places and orient themselves suitably to fit in more exactly as there is more time available. The result is a small well formed, more perfect crystal with well defined boundaries, smooth faces and a symmetrical twin pattern. The presence of smaller perfect crystals occurring either separately or as cores in 23/952, probably represent the few earlier, small perfect crystals in 23/951 which have grown at a moderate pace keeping as perfect as possible, as pointed out earlier.

It seems quite clear that the crystals of type II and III are results of growth in the labile stage and the perfect, well-formed crystals of type I probably of the metastable stage; but it is not quite definitely known to which stage, the growth of the large, irregular crystals of type IV in specimen 23/952, should be ascribed. It is also very likely that during the later stages of cooling the conditions of crystallization alternated between the metastable and labile states probably due to the heat liberated by rapid crystallization and the changes in molecular concentration. Chevalier (11) has shown that these different states can even coexist in the different parts of a single drop due to the changes in molecular concentration by rapid crystallization. The persistence of the skeletal crystal clusters (though slightly larger in size) in specimen No. 23/952 and the presence of smaller, perfect crystals support this alternation of the labile and metastable states to some extent. The inclusion of spherulitic growths, characteristic of labile state (11), in the large irregular crystals of type IV and the enveloping of the small perfect crystals of type I by spherulitic growths are also in favor of the above suggestions. It is however, inexplicable that the spherulites are rare in specimen 23/951.

We have therefore reasons to believe that the smaller, more symmetrical and perfect crystals grew slowly, probably in the metastable state while the large irregular hexagonal crystals with multiple terminations grew very rapidly and that the skeletal crystal clusters and wreaths represent growth in the labile state. A more detailed picture of the various physico-chemical factors relating to the formation and growth of these crystals, will have to depend on more precise knowledge of other data besides the mere shape, size and perfection of crystal grains.

DIFFERENTIAL RATE OF GROWTH

From the foregoing description of the growth and shape of the crystals, it can be seen very easily that a growing crystal has certain preferential directions along which growth takes place more easily and quickly as is specially brought out in the rapidly grown crystals. The long, slender pencil-like, hollow crystals forming bundles in types II and III and the general elongation of the prisms parallel to the *c* crystal axis in almost all crystals of cordierite, the arms in the tentacled hexagons, the secondary branches from these arms, and the spirals and rings, all indicate these directions of rapid growth. The following are the preferred directions of growth from the centre:

(*a*) towards the solid angles of the pseudohexagonal prism i.e., where the prism edges meet the base, as shown by the step wise growth of prisms along their corners and the hollow transversely elongated bobbin or *H* shaped skeletal crystals (Pl. II, Figs. 2, 21 and 22);

(*b*) towards the edges of the prisms i.e., the corners of the hexagonal outline as seen in basal sections (Figs. 10, 11, 13, 14 and 15); and

(*c*) parallel to the sides of the hexagon which is also a parallel direction to *b*. The secondary branches from the arms of the tentacled hexagon (Figs. 9, 10, 11, 14 and 17) and the spirals and rings (Figs. 3, 4, 5, 7, 8, 9) exhibit this tendency very well.

This leaves one significant direction towards which growth is very slow and sluggish i.e., towards the prism face or hexagonal side, which consequently shows embayments or enclosures.

The general prevalence of the hexagonal motif in all the crystal forms of cordierite described here and the preferred growth in particular directions, may probably be explained as being the characteristic manifestation of the crystal structure of cordierite. Gossner and Mussgnug (cited by Bragg and Bystrom), perhaps the first to investigate the crystal structure of cordierite, suggested a psuedohexagonal structure of the beryl type for the mineral, from the facts that the formula written as $Mg_2Al_4Si_5O_{18}$ was similar to that of beryl and the ratio $a:b$ was close to $\sqrt{3}$. Bragg (4) has supported this view and writes the formula as $Al_3Mg_2(Si_5Al)O_{18}$, and recently Bystrom (9) has further confirmed the close similarity between the orthorhombic (pseudohexagonal) structure of cordierite and the hexagonal structure of beryl. While on the structure of beryl which shows such close similarity to that of cordierite, Bragg and West (5) observe that the hexagonal rings formed by the six silicon oxygen tetrahedra are stacked on each other along the hexagonal axis forming a series of open channels parallel to the *c* crystal axis. This honeycomb-like arrangement and the striking open channels in the structure, they remark, might confer on the crystal some special properties. Folinsbee (16) makes particular reference to these hollow central channels in the structure as possible spaces for the location of alkalies, in discussing the variability of optic properties of cordierites in relation to their alkali content. Bystrom also recognizes these channels as the probable spaces for the location of water and alkalies. It is now interesting to note the remarkable extent to which the hollow, slender needles and the spirals and rings, simulate and reflect the structural peculiarities.

It is well known that the different crystal faces of a particular mineral have different rates of growth indicating the difference in the ease with which molecules can slip into their places on different growing faces. This is sometimes influenced by the difference in force of molecular attraction or cohesion in different directions—evidenced by the differential bonds in the case of bismuth and its homologues—as observed by Bragg (3) who further remarks that "without a more detailed knowledge of the active forces localised at various points of atoms and molecules, we cannot build up a complete theory of cohesion." No attempt is being made in this paper to show the exact nature of the interatomic or molecular forces in different directions in the cordierite structure which may influence this differential rate of growth. It is also not known whether such nonuniform bond density exists in cordierite or not.

Besides the unequal bond strength in different directions controlled by the peculiarities of atomic structure, other explanations are also possible for this preferred growth of cordierite in particular directions. These explanations of course are also ultimately related to the structural pattern in the crystal.

Buerger (8) has attempted to explain the relative ease of growth of crystal faces by such considerations as co-ordination and surface energy. It is shown that the preferred site is the one which affords the greatest decrease in surface energy for the incoming molecules. In other words, a preferred site affords a molecule the greatest total coordination or greatest bonding energy which is complementary to surface energy. This would of course be modified and influenced by the location and strength of strong bonds in a molecule or atom possessing non-uniform bond density (as in bismuth?).

In seeking an explanation for the cause of mineral incrustations upon the corners and edges of crystals, Frondel (17) remarks that these are the parts of a crystal having greater adsorptive powers and the cause for this is sought from the work of Taylor (27) on metallic hydrogenation catalysts. Taylor states that, "the atoms in the edge of a granule have one less degree of saturation than those in the surface proper; atoms at a corner have two less than those in the surface and one less than those at an edge." Preferred adsorption or growth at corners and edges of a crystal are thus caused by the low degree of saturation of the atoms or molecules placed at these points.

This rapid rate of growth along the corners and edges of a crystal is not wholly dependent on the peculiarities of crystal structure and it is more likely to be a general result of the low degree of saturation at these points as explained by Taylor, and all rapidly grown crystals should show similar growth irrespective of their crystal structure. In this connection it is pertinent to quote the observations of Flett (15) concerning the unequal growth of augite in some Scottish buchites: "Very often the corners of the crystals have grown outwards so rapidly as to form projecting spikes while depressions correspond to centres of pinakoidal faces."

During the early stages of growth of a crystal, there are certain thermal stresses set up on the surface of the crystal due to factors such as the latent heat of crystallization (Zwicky), impurites (Buerger), etc. This would lead to the formation of certain cracks (referred to as Zwicky cracks) whose spacing and width are mostly a function of the atomic structure of the crystal. These cracks would cause irregularities and slight deviations in the orientation of the different growth layers on the blocks bounded by these cracks, the final result being the development of lineages or block structure in crystals (6 and 7). The orientations of the lineages or blocks descend continuously from a parent nucleus but differ mutually, the degree of difference being proportionate with the distance from the nucleus. Buerger (6) observes that crystals in parallel positions and dendrites are special cases of lineage growth and form by more rapid rate of growth. He says "The essential difference between simple lineages and exaggerated cases of parallel growth is that in the former the structure is bathed by a solution of more or less uniform concentration on all sides, so that the space between the lineages is kept filled with precipitated material and the lineages are able to keep pace with the growth of one another while in the latter case, the rapid growth allows material to be added only to the growing ends of the separated lineages, the region of interlinear boundaries not receiving much material for growth because it is all precipitated on the leading tips." The interlineage boundaries obviously form the loci for negative crystals or cavities.

Davey (12) has also drawn attention to the rapid needle-like outgrowths from the corners of blocks formed by the intersection of the Zwicky cracks, resulting from the least potential energy at these spots which helps to hold tightly the incoming material. The development of these needle-like outgrowths are common in the earlier stages of all rapidly grown crystals. The interspaces between this net work of needles are filled at a later stage to form single, smooth faced crystals. These needle like skeletons probably correspond to the initial stages of Buerger's lineages.

The figures of spectroscopically pure zinc grown from vapor, given by Davey show fin-like outgrowths branching off from the stem at angles of 30° and 60° characteristic of the hexagonal close packed structure of zinc. These fins represent later stages of growth of the secondary and tertiary needle-like projections from a growing surface. The figures closely resemble some of the cordierite crystals of type IV. So, it appears quite likely that these projections and outgrowth on a large, quickly grown cordierite grain would be caused by the Zwicky cracks and development of lineages.

Thus the sites of rapid growth are more likely to be conditioned by simple, general considerations such as surface energy, total co-ordination, degree of saturation and development of lineages than by the peculiarities of the atomic structure. This contention is supported by the similar shapes of skeletal crystals, of parallel growths, of rapidly grown grains and of dendrites in different minerals. The ultimate influence of the distinctive atomic structures of different minerals, in determining the angular relations, location and number of the sites of easy and quick growth cannot however be disregarded.

Twinning and Its Relation to Growth

A genetic relationship between twinning and mode of growth in these cordierite crystals is apparent as the latter is the most important if not the sole controlling and modifying factor of the former. Two general types and patterns of twinning—the 'radial' giving rise to sixlings and stars, and the 'concentric' with twin lamellae mostly parallel to the hexagonal sides—are recognized (30). Combinations of both are also observed.

The sixlings (trillings are very rare) and star shaped (with twelve pointed rays) twins are generally associated with the smaller, well-formed, symmetrical individual crystals. There is no cavity or inclusion at the centre and the nucleus itself starts as a twinned individual and encouraged by slow, steady and orderly growth, a perfect radial twin pattern is built. In rapidly grown crystals of bigger sizes this orderliness, or symmetry, is partly lost due to lack of time for proper orientation of the added material, and an unsymmetrical confused pattern of twinning is produced. The sixlings are almost always twinned on (110) planes which connect the corners of the hexagonal outline. A twelve pointed star is produced by the presence of (130) twin planes in alternate positions with the (110) planes.

A concentric twin pattern on the other hand is very characteristic of cordierite developed from skeletal crystals, spirals and rings. Here the crystal growth does not proceed methodically and equally in all directions, but in preferred directions which are usually parallel to the hexagonal sides and thereby promoting the development of concentric twin lamellae parallel to the hexagonal faces or sides. They develop so naturally in a hollow ring, or spiral, or an outgrowth building the prism faces, all of which grow in directions parallel to the twin lamellae. A few radial twin planes may also get formed normal to, or at high angles to, the prism faces, possibly due to the meeting of two growing surfaces; but the predominant pattern is still concentric.

In a few cases growth may be slow and moderate in the early stages giving rise to a star shaped twin around which a concentric or irregular pattern may develop as the growth becomes rapid. Glassy enclosures and cavities are common in these rapidly grown concentric or irregular twins, but not in the slowly grown radial and star shaped twins.

Thus the twin pattern is fully conditioned and controlled by the mode and speed of growth, yielding small symmetrical radial twins or concentric or irregular patterns of poor symmetry. In para-lavas which have formed by fusion and quick cooling, the duration of conditions suitable for crystal growth is short and hence all the large grains have grown very rapidly causing imperfections and distortions in the symmetry of twin patterns. But in a magmatic or metamorphic environment, conditions favoring crystal growth may be very prolonged and large crystals with beautiful and symmetrical twinning may be produced even with moderate and slow rate of growth. Such crystals are, however, not very common even under the latter conditions.

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WARDITE FROM BERYL MOUNTAIN, NEW HAMPSHIRE*

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ABSTRACT

Wardite in well-formed, white to colorless crystals has been found in a pegmatite at Beryl Mountain near West Andover, New Hampshire. Tetragonal-pyramidal, $P4_1$. The forms present are: $c\{001\}$, $a\{010\}$, $m\{110\}$, $u\{011\}$ and $t\{012\}$. $a_0=7.04$ Å, $c_0=18.88$ Å; $a{:}c=a_0{:}c_0=1{:}2.6818$. Composition: Al_2O_3 38.70, FeO 0.26, MgO 0.21, Na_2O 7.51, K_2O 0.16, P_2O_5 35.12, H_2O 17.88, which gives the formula $NaAl_3(PO_4)_2(OH)_4\cdot 2H_2O$, with 4 formula weights in the unit cell. G = 2.81 measured and calculated. nO = 1.5940, nE = 1.6040 ±0.0005.

Active mining of beryl at Beryl Mountain near West Andover, New Hampshire, during the past few years has uncovered several interesting minerals. The most unusual for this pegmatite is a single specimen composed mostly of quartz with an area on one side about 10×15 centimeters, coated with white to colorless crystals of wardite. This is the third locality for wardite. The original description was by Davison (1896) of material from Fairfield, Utah. Wardite from the same locality has subsequently been studied by Larsen and Shannon (1930), Pough (1937), and Larsen (1942). The mineral soumansite, described by Lacroix (1910) from Montebras, France, was shown by Larsen and Shannon to be identical with wardite.

Morphology. The Beryl Mountain wardite is in well-formed crystals ranging from 1 millimeter to 10 millimeters in a maximum dimension. These crystals are much larger than those earlier described; the largest crystals from Fairfield are slightly over 1 millimeter in maximum dimension. The Beryl Mountain crystals are similar to those described by Pough (1937) and are dominated by the pyramids $\{012\}$ and $\{01\bar{2}\}$ as shown in Figs. 1 and 2. Some crystals show sharp signals from the faces of $\{011\}$ and $\{012\}$ whereas others give a continuous signal train between the faces of these two forms. Although $\{010\}$ is more commonly present than $\{110\}$, the faces are of poorer quality than those of the first-order prism. Pough did not observe $\{110\}$ on Fairfield crystals; none of the forms he considered doubtful was found on crystals from Beryl Mountain. Although the crystal class is tetragonal-pyramidal, the crystals are symmetrically developed with the same forms at opposite ends of the c axis.

From single crystal x-ray measurements Larsen (1942) calculated the axial ratio as $a_0{:}c_0=1{:}2.6818$. Pough, by taking the c value as one half the true unit, calculated from morphological measurements: $a:c = 1:1.3117$. Larsen made the reasonable assumption that the ratio from *x*-ray data was more accurate than that derived from morphology because of the " . . . poor quality of the crystals and the great range of Pough's measured values." The transformation of Pough to Larsen (100/010/002) gives for Pough's dominant form, *t* {0.13.12} the symbol {0.13.24}. Larsen assumed that this should probably be {102} and calculated for it the ρ value using his axial ratio.

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 333.

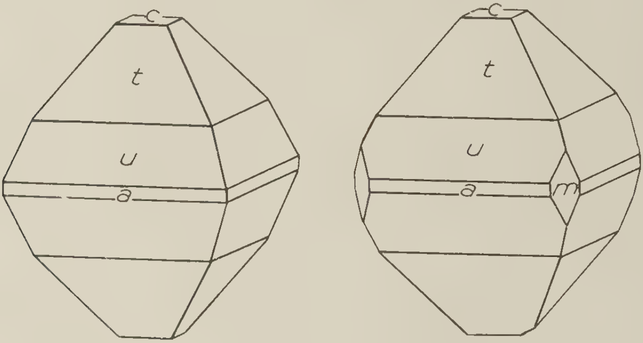

Fig. 1 Fig. 2

Wardite crystals, Beryl Mountain.

In the present study seven of the best wardite crystals from Beryl Mountain were measured on the two-circle goniometer. The results are given in Table 1.

Table 1. Wardite—$NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$, Tetragonal-pyramidal—$P4_1$
(measured and calculated angles)

Form	No. of faces	Measured range	Measured mean	Calculated angles*	
		ρ	ρ	φ	ρ
c 001	7	—	—	—	0°00′
a 010	8	—	—	0°00′	90 00
m 110	6	—	—	45 00	90 00
u 011	6	69°12′–69°52′	69°35′	0 00	69 33
t 012	21	53 7–53 38	53 20	0 00	53 17

* From Larsen (1942) with $p_0 = 2.6818$ and $a:c = 1:2.6818$.

It will be noted that the measured ρ of *t* {012} is close to the calculated value and proves that this is the true symbol as assumed by Larsen. Weissenberg photographs of Beryl Mountain wardite proved to be identical to those taken by Larsen on a Fairfield crystal. The cell dimensions: $a_0 = 7.04$ Å ± 0.02, $c_0 = 18.88$ Å ± 0.02 yield the ratio $a_0 : c_0 = 1 : 2.6818$. Although the crystals from Beryl Mountain are of much better quality than those from Fairfield, it seems unwise to use their measurements to introduce a new morphological axial ratio but rather to assume as correct, for both unit cell and morphology, the ratio given above.

Chemical composition. A chemical analysis of wardite from Beryl Mountain was made by F. A. Gonyer in connection with the present study. It is given in Table 2 with two earlier analyses.

TABLE 2. CHEMICAL ANALYSES OF WARDITE

	1	2	2*a*	3	4	5
Al_2O_3	38.25	36.54	36.6	38.25	38.70	38.43
FeO	0.76	—	—		0.26	
CaO	—	3.30	3.0	none	—	
MgO	2.40	—	—	.33	0.21	
CuO	0.04	—	—		—	
Na_2O	5.98	6.68	7.0		7.51	7.79
K_2O	0.24	0.73	0.6		0.16	
P_2O_5	34.46	34.76	34.9	34.58	35.12	35.68
H_2O	17.87	17.85	17.9		17.88	18.10
	100.00	99.86	100.0		99.84	100.00
Sp. Gr.	2.77	2.81			2.81	2.81

1. Davison (1896)—Fairfield, Utah.
2. Shannon (Larsen and Shannon, 1930)—Fairfield, Utah.
2a. Analysis 2 corrected for impurities.
3. Gonyer—(Partial analysis), Fairfield, Utah.
4. Gonyer—Beryl Mountain, New Hampshire.
5. Calculated composition: $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$.

The above table shows striking differences in analyses of wardite from Fairfield, Utah; Davison giving MgO = 2.40 per cent with no CaO and Shannon giving CaO = 3.30 per cent with no MgO. Larsen and Shannon state that Davison's analysis " . . . was probably made on a less pure sample." In order to determine which of these analyses is more probably correct, Gonyer made a partial analysis of Fairfield wardite. He found no CaO and only 0.33 per cent of MgO. The analysis, therefore, checked neither of the earlier ones but did agree closely with the analysis of wardite from Beryl Mountain.

In Table 3 the analysis of Beryl Mountain wardite is given recalculated to 100 per cent. Using these percentages and the molecular weight of the unit cell (1593), the number of atoms in the unit cell was calculated and is given in column 4. If it is assumed that these numbers represent the integers 12, 4, 8 and 32, respectively, the composition of wardite can be written as: $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$ with 4 formula weights in the unit cell. Larsen (1942) wrote the formula based on the analysis of Shannon as: $CaNa_4Al_{12}(PO_4)_8(OH)_{18} \cdot 6H_2O$. However, the the specific gravity calculated for this formula and the unit cell volume is 2.87. Using the same volume for the unit cell, but with the formula, $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$, the calculated specific gravity is 2.81. This agrees exactly with the measured specific gravity of wardite from Beryl Mountain as well as that from Fairfield, Utah, as reported by both Larsen and Shannon (1930) and Larsen (1942).

TABLE 3. WARDITE: ATOMS PER UNIT CELL

	Analysis 4 of Table 2 reduced to 100 per cent	Molecular ratios	Atomic ratios	Atoms/unit cell
Al_2O_3	38.76	.3802	.7604	12.1
FeO	0.26	.0036	.0036	
MgO	0.21	.0052	.0052	
Na_2O	7.52	.1139	.2278	3.8
K_2O	0.16	.0017	.0034	
P_2O_5	35.18	.2477	.4954	7.9
H_2O	17.91	.9950	1.990	31.6
	100.00			

Optical Properties. The optical properties of wardite from Beryl Mountain compared with those of wardite from Fairfield, Utah (Larsen and Shannon) are:

	Beryl Mountain		*Fairfield, Utah*	
*n*O	1.5940	±.005 uniaxial (+)	1.590	±.005 uniaxial (+)
*n*E	1.6040		1.599	

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A NEW SERIES OF IMMERSION LIQUIDS*[a]

Robert Meyrowitz

Abstract

A new series of high-index immersion liquids (1.66–1.81) has been made. α-bromonaphthalene and a solution of precipitated sulfur (10 per cent) in arsenic tribromide are the end members. The mixing curve is not a straight line. After nine months the maximum change in index was -0.001. Stable liquids containing α-bromonaphthalene, arsenic tribromide, precipitated sulfur, and arsenic disulfide are discussed.

Introduction

A study of inorganic, organic, and metal-organic compounds that might be employed in the preparation of liquids of high refractive index is in progress at the U. S. Geological Survey. It is part of a program of research in the geochemistry of uranium that the Geological Survey is undertaking on behalf of the Atomic Energy Commission.

In a previous paper (Meyrowitz and Larsen, 1951) describing immersion liquids of high refractive index, a series of liquids containing methylene iodide, arsenic tribromide, and precipitated sulfur was introduced. The indices of refraction of this series range from 1.74 to 1.81. It was reported in that paper that these liquids darkened on standing because of the decomposition of methylene iodide. Nevertheless their indices of refraction have remained nearly constant for 15 months. As the decomposition seemed to be continuing, work was begun immediately on the development of a new set of immersion liquids in the range of 1.74 to 1.81, not containing methylene iodide. It was found that α-bromonaphthalene could be substituted for methylene iodide in these liquids.

The liquids made of α-bromonaphthalene and a 10 per cent solution of precipitated sulfur in arsenic tribromide have been used for nine months. They have shown no decomposition, and their indices of refraction have remained nearly constant. They may replace the methylene iodide liquids.

The new liquids are light yellow and after a period of nine months the maximum change in index was -0.001. They are stored in glass bottles with ground-glass stopper and a ground-glass dust cover. The 1.80, 1.81, and 1.82 liquids may become solid if the temperature at which they are stored falls much below that of normal room temperature (20 to 25° C). Gentle warming will effect complete solution and after thorough mixing the clear liquid will have its original refractive index.

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[a] This report concerns work done on behalf of the U. S. Atomic Energy Commission and is published with the permission of the Commission.

The temperature coefficient (dn/dT) and the dispersion as measured by the difference in index between the "e" line of mercury (546) and the "D" line of sodium (589) are as follows:

	dn/dT	*Dispersion*
α-bromonaphthalene	4.8×10^{-4} (Larsen and Berman, 1934)	76×10^{-4}
10 per cent sulfur in arsenic tribromide	6×10^{-4}	114×10^{-4}

PREPARATION OF IMMERSION LIQUIDS

Reagents

(1) α-bromonapthalene, Eastman Organic Chemical no. 46, supplied by Distillation Products Industries, Rochester 3, N. Y.
(2) Sulfur, precipitated, U.S.P.
(3) Arsenic tribromide, C. P., supplied by A. D. Mackay, Inc., 198 Broadway, New York 7, N. Y.

The end members are:

(1) α-bromonaphthalene, $n_{Na}^{25^\circ C}=1.655$
(2) 10 per cent sulfur in arsenic tribromide, $n_{Na}^{25^\circ C}=1.814$.

The sulfur and arsenic tribromide (10 to 90 by weight) are mixed in a glass-stoppered Erlenmeyer flask, and solution is effected by gentle warming. After standing at room temperature overnight, the solution is filtered by suction through a sintered glass of "medium" porosity.

10 per cent S in $AsBr_3$ (in grams)	α-bromonaphthalene (in grams)	$n_{Na}^{25^\circ C}$
28	272	1.662
69	231	1.673
88	212	1.679
118	182	1.690
142	158	1.700
163	137	1.710
184	116	1.721
200	100	1.729
216	84	1.739
233	67	1.752
244	56	1.760
256	44	1.769
268	32	1.780
276	24	1.788
287	13	1.799
296	4	1.809

TABLE 1. CHANGE IN REFRACTIVE INDEX OF LIQUIDS CONTAINING α-BROMONAPHTHALENE, ARSENIC TRIBROMIDE, SULFUR, AND ARSENIC DISULFIDE AFTER A PERIOD OF NINE MONTHS

Number	$n_{\mathrm{Na}}^{25^\circ\,\mathrm{C.}}$ (initial)	$n_{\mathrm{Na}}^{25^\circ\,\mathrm{C.}}$ (after nine months)	$\Delta n \times 10^{-3}$ (9 months)	$n_{\mathrm{Na}}^{25^\circ\,\mathrm{C.}}$ of high end member ($AsBr_3$—S—AsS)
1	1.666	1.665	−1	1.924
2	1.672	1.672	0	1.924
3	1.683	1.683	0	1.924
4	1.692	1.691	−1	1.924
5	1.706	1.705	−1	1.924
6	1.719	1.718	−1	1.924
7	1.738	1.737	−1	1.924
8	1.750	1.749	−1	1.924
9	1.773	1.771	−2	1.924
10	1.792	1.791	−1	1.924
11	1.822	1.820	−2	1.924
12	1.848	1.846	−2	1.924
13	1.887	1.885	−2	1.982
14	1.923	1.921	−2	1.982
15	1.938	1.937	−1	1.982
16	1.968	1.966	−2	1.982
17	1.868	1.866	−2	1.999
18	1.897	1.896	−1	1.999
19	1.957	1.956	−1	1.999
20	1.979	1.977	−2	2.027
21	2.003	1.998	−5	2.027
22	2.018	2.015	−3	2.027

The filtrate is passed through the same filter until it is no longer turbid.

The mixing curve obtained with the two end members deviates considerably from a straight line, and the curve may be constructed from the table at the foot of the preceding page.

The necessary amounts by weight of the high and low end members are mixed together in glass-stoppered bottles or Erlenmeyer flasks to obtain the series of liquids of desired intervals. The refractive indices of the liquids are determined after thorough mixing.

Experiments indicate that a discontinuous series of liquids containing α-bromonaphthalene, arsenic tribromide, arsenic disulfide, and precipitated sulfur can be made. These liquids range in index from 1.66 2.02. This discontinuous series of liquids can probably be made up of two continuous series of liquids with α-bromonaphthalene as the lower end member and two solutions both containing arsenic tribromide, sulfur, and arsenic disulfide in different proportions as high end members.

High end members with indices of 1.922, 1.936, 1.945, and 1.956 were used to make liquids with a refractive index of 1.660 that have remained stable for six months. If stable liquids at the low end of the series can be made, then it should be possible to produce a stable continuous series of liquids, as demonstrated by liquids 1 to 12 in Table 1. Stable liquids of refractive index 1.66 could not be prepared by adding α-bromonaphthalene to liquids of very high refractive index ($n=1.982$ and 1.999) containing arsenic tribromide, sulfur, and arsenic disulfide.

The gap between 1.95 and 2.02 has been filled by using high end members with refractive indices of 1.999 and 2.027. Although a series from 1.66 to 2.02 can be made by using three high end members, the author is attempting to develop two high end members from which the entire series from 1.66 to 2.02 can be produced.

The stability of the liquids containing α-bromonaphthalene, arsenic tribromide, sulfur, and arsenic disulfide is shown in Table 1.

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NOTES AND NEWS

CRYSTALLOGRAPHIC PROJECTIONS NOMENCLATURE DILEMMA

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Abstract

The terms stereographic and gnomonic refer to direct projections in their original and current cartographic meanings. It is suggested they be used in this sense by crystallographers, and that the latter designate their polar (reciprocal) variants as verstereographic and antignomonic respectively.

The stereographic projection has been known and used by astronomers, cartographers, and navigators since Ptolemy (probably derived from Hipparchus). It was given its present name in 1613 by Aguilonius. The gnomonic projection[1] may have been known to Ptolemy (according to Delambre), but apparently it was described first a millennium and a half later, by Grienberger in 1612. Originally used for star maps, later it became important for terrestrial maps to facilitate great circle navigation and avigation. These historical remarks are abstracted from Hutchinson (1908, pp. 105–112).

Except in crystallography these projections were always *direct* ones; that is, the element itself was projected; not its normal. Thus a *line* on a sphere such as a meridian on the globe (a spherical projection of the earth) became a *line* on the map or projection. A central plane intersects a sphere in a great circle; the meridians on a globe are examples. In crystallography such a great circle is often represented by a "pole," or point where the end of a radius of the sphere of projection normal to the plane in question is projected. Such a projection is *reciprocal;* instead of projecting the element itself, one projects its normal.

These projections were first taken over into crystallography by Franz Neumann in 1823. Most of his *Beitraege zur Kristallonomie* is devoted to a development of "the projection" (he nowhere refers to it as gnomonic; it is unlikely that he knew this term) and its crystallographic value. He emphasizes the use of a "gerade Endflaeche" (we would say a plane normal to the *c*-axis) as the plane of projection (even in the monoclinic), but devotes the last portion of Section 4 of Part 1 to the projection of isometric forms on other planes. He considers face-directions (the normals to crystal faces; the directions of growth) and zone-planes (planes normal to zone-axes) as of far greater significance than crystal faces and zone axes. He thus projects what we would consider reciprocal elements, which is the antithesis of previous practice: "so wird *unsere* Betrachtungsweise gleichsam als die *invertierte* von der bisher ueblichen zu bezeichnen sein; sie ist im eigentlichen Sinn ihr Gegenstueck" (Carl Neumann, 1916, p. 349; slightly different in E. R. Neumann *et al.*, 1928, p. 287). Here indeed is the first recognition of the germ of the reciprocal lattice idea, a concept that lay fallow for a generation or more; until Bravais (1850) introduced his *polar* lattice (see Shaler. 1949, p. 92), and his pupil Mallard (1879) and later Goldschmidt (1886, 1887) tied this back to the gnomonic projection. Neumann speaks of the projected elements as zone-lines and face-points (Flaechenorte); indeed the latter are marked by symbols that are substantially the same as the Goldschmidt indices (1916, Pl. IV; 1928, Fig. 9, p. 204). In an appendix he states that one can also project crystal faces as face-lines, and a zone-axis as a zone-point (Zonenort); but this he obviously considers to be of little importance. He notes that all the face-lines of a single zone intersect at the zone-point, and all the zone-axes in a single plane have zone-points which lie on the face-line of that plane.

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[1] Germain, A. (1865?), Traité des Projections, Paris, states (pp. 122–123): "The origin of this (gnomonic) projection, the oldest known, seems to go back before Thales of Miletus, the predictor of eclipses, who died in 548 B.C. Called successively by the names of 'horoscope' and 'analemme,' it was much used in astronomy under the name of 'gnomonic' to trace the course of celestial phenomena from the surface of the earth." This quotation was kindly furnished me by the Director of the U. S. Coast and Geodetic Survey (June 5, 1952). *Sp. Publ. No.* 68 of this organization on the "Elements of Map Projection" is a most successful elementary treatment of the subject.

While Franz Neumann made only minor use of the stereographic projection (which he referred to as the spherical surface) in his 1823 work (see 1916, Pl. VI; 1928, Figs. 20 and 28), he emphasized it in his 1825 paper on axinite (1928, p. 368). However, according to Barker (1922, p. 90) this "projection was eventually taken up and adapted to a remarkably simple and symmetrical form of logarithmic treatment by Miller, with results that are familiar to all." Actually Miller made great use of spherical trigonometry in crystal calculations; he spoke of (face) poles on the surface of the sphere of projection in his 1863 "Tract," which does not have the word *stereographic* in it; though in the preface he refers to two of his papers in the *Philosophical Magazine* (**18**, 1859, 37–50; and **19**, 1860, 325–28) which treat the gnomonic and stereographic projections.

Thus while these two projections were introduced into crystallography by Neumann when still a poverty-stricken 25-year old student under Weiss at Berlin, and only four years after he started in this field of endeavor, others pushed them into crystallographic prominence. In fact Johannsen (1918, p. 5) notes that Neumann's book does not appear to have been appreciated, since only the first part of it was issued (during his lifetime). The book had three parts according to C. Neumann (1916), who included F. Neumann's doctorate thesis as Part III; this last is put as a separate paper by E. R. Neumann *et al.* (1928), thus leaving but two parts. In fact these latter two "reprints" differ from each other, and probably also from the original (which has not been seen by the present writer) in many respects. An exact reprint would be very difficult for the modern reader to interpret; even Groth (1926, p. 78) found this to be true. In Franz Neumann's youth the science was in its infancy.

Goldschmidt (1886, p. 3) carefully distinguished between polar (reciprocal) and direct projections, and introduced the term *cyclographic* for the direct form of the stereographic projection, which latter he regarded as a polar projection (as Neumann had indeed used it). At this time he spoke of *linear* as the direct version of the gnomonic, but later (1887, p. 3) introduced the term *euthygraphic* for this, to avoid confusion with Quenstedt's linear projection (see Rogers, 1937, pp. 30, 47). In general Goldschmidt's terminology has been employed up to the present see Fisher, 1952, pp. 84–85).

In handling these projections in a course on structural geology, where maps are so important, this fundamental misuse of the terms stereographic and gnomonic struck the writer very forcibly. Since the structural geologists (Bucher, 1944; Nevin, 1949, pp. 379 -391) are now beginning to make considerable use of these projections, it is time to redefine the terms used in crystallography to fit the original cartographic meanings. Thus, we must employ the terms stereographic and gnomonic for direct projections, and coin new ones for their reciprocal variants.

We could speak of the polar stereographic/gnomonic, or we could use reciprocal, inverse, or anti- in place of polar. The word polar is not good, since it is too easily confused with face-poles or zone-poles (edge-poles), terms in standard use. For the same reason I am against costereographic and cognomonic, since just as we speak of *ster-* and *gnom*-points (Fisher, 1952, p. 86), it is often handy to refer to *coster-* and *cognom* points. The word reciprocal is too long. The terms *verstereographic* and *antignomonic* are thus suggested for the reciprocal (polar) variants of the stereographic and gnomonic projections. It is better not to use the same prefix to designate these two variants, because it is often handy to employ one-letter symbols on a combined projection (gnomonostereogram). Thus, on such a projection one may use ⊡ $[uvw]^{s}$ or ⊡ $[uvw]^{g}$ for zone-poles and $[uvw]^{v}$ or $[uvw]^{a}$ for zone-lines. Similarly ⊙ $(hkl)^{v}$ or ⊙ $(hkl)^{a}$ symbolizes a face-pole and $(hkl)^{s}$ or $(hkl)^{g}$ a face-line.

In view of these considerations the writer (see Fisher, 1952, p. 84) would like to submit a revised Table 2.

Goldschmidt's terms were unsatisfactory not only because they tended to freeze crystallographic usage into a terminology that was contrary to the historical meanings of the older words, but also because there was no obvious connection between euthygraphic-gnomonic and stereographic-cyclographic. The suggested new terminology avoids both of these defects. Professor J. D. H. Donnay[2] prefers to speak of direct and polar stereographic or gnomonic (or spherical), and not introduce new terms. After all, the projections remain what they are, regardless of whether an element or its normal is projected. "The chief trouble with the other names is that they make people believe that the projections are different in principle, whereas they differ only by *what we project.*"

REVISED TABLE 2. DIRECT AND RECIPROCAL PROJECTIONS

Element to project	Type of Projection	
	Direct (*primitive*) Stereographic or Gnomonic	*Reciprocal* (*polar*) Verstereographic or Antignomonic
Zone axis (or other *direction*)	ZONE POLE (a point) Symbol $[uvw]^s$ or $[uvw]^g$	ZONE LINE (a great circle) Symbol $[uvw]^v$ or $[uvw]^a$
Crystal face (or other *plane*)	FACE LINE (a great circle) Symbol $(hkl)^s$ or $(hkl)^g$	FACE POLE (a point) Symbol $(hkl)^v$ or $(hkl)^a$

This is a most pertinent statement; it is true for the Goldschmidt terms. If one wishes to project a bedding plane or a fault plane, is it better to refer to the plane in the projection as verstereographic/stereographic or as polar stereographic/direct stereographic? In settling this question it should be remembered that crystallographers and structural geologists will likely be dealing with the same students; the choice of proper use of terms cannot be decided on satisfactorily with a limited point of view. Properly speaking the stereographic projection of a bedding plane is a projected great circle; not a "bedding-pole." Unfortunately it has become common crystallographic usage to speak of a face-pole (a point) as the stereographic (or gnomonic) projection of the face, and it may be difficult to change this. The thesis of this paper is that it is better to do it now rather than later. Clear thinking is essential, especially when we complicate our projections by adding cleavage and optical directions and planes to those of morphological crystallography; thus precise terminology without conflicting meanings becomes fundamental.

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[2] Personal communication, June 7, 1952.

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UNIVERSAL COMPASS AND THE PLUNGE OF THE BEDDED CUPRIFEROUS PYRITIC ORE DEPOSIT IN JAPAN

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In 1942, Earl Ingerson[1] devised a universal compass in order to measure the angle and direction of pitch of lineation in the field. In 1943, Ingerson and Tuttle[2] drew a graph, which is convenient for the determination of a lineation in the plane of schistosity. Also, D. J. Fisher[3] proposed the stereographic and gnomonic solution of the lineation. K. E. Lowe[4] described another geometrical method of determination.

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[1] Ingerson, Earl, Apparatus for direct measurement of linear structures: *Am. Mineral.*, **27**, 721–725 (1942).

[2] Ingerson, Earl, and Tuttle, O. F., A graph for determining angle and direction of pitch of lineations in the field: *Am. Mineral.*, **28**, 209–210 (1943).

[3] Fisher, D. Jerome, Measuring linear structures on steep-dipping surfaces: *Am. Mineral.*, **28**, 204–208 (1943).

[4] Lowe, K. E., A graphic solution for certain problems of linear structure: *Am. Mineral.*, **31**, 425–434 (1946).

In Japan, the determination of linear schistosity is important from the point of prospecting of the bedded cupriferous pyritic deposits in the crystalline schists and phyllites. In southwestern Japan a zone of metamorphic rocks extends along the "Median Tectonic Line," which runs from northeast to southwest (Fig. 1). The rocks are composed of albite epidote chlorite schist, amphibole chlorite schist, glaucophane schist, piedmontite quartz schist, stilpnomelane-bearing green schist, graphite quartz schist, sericite quartz schist, graphite phyllite, etc. intruded by amphibolite, meta-diabase schist, meta-diabase and serpentine. Throughout this elongated area, many deposits of cupriferous pyrite occur along the planes of schistosity, commonly as lenticular or bedded deposits. The largest deposit of this type is that of the Besshi mine, which has a strike length of more than 1600 m., extends over 1000 m. down the dip and is up to 10 m. thick. The mineralizing solution may have originated in the same deep seated magma from which the basic and ultrabasic rocks such as amphibolite, meta-diabase and serpentine were derived. No particular type of schist constitutes the sole host rock, but green-colored schist is more common. It is noticeable that a lens of piedmontite quartz schist is sometimes accompanied by an ore body.

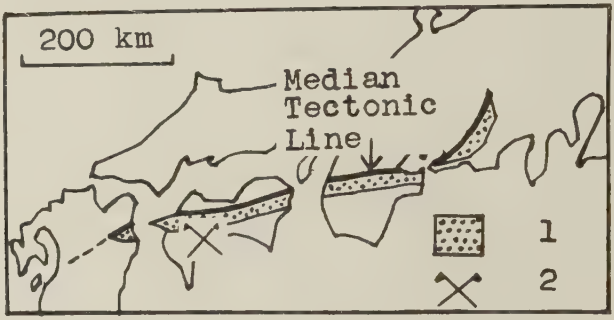

FIG. 1. Index map. 1. Crystalline schists and phyllites. 2. Besshi mine.

A critical feature is that the ore bodies have the direction of elongation parallel to the orientation of the elongated minerals and of the microfolding in the host rocks and it is of great value in predicting the direction of plunge of ore shoots.[5] This direction also coincides with the axis of folding (Fig. 2).

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[5] This fact was described by E. Sagawa in 1910 [Résumé of a report on the geology of the cupriferous pyrite deposits in the crystalline schists of the northern part of Awa and northwestern part of Iyo in the Island of Shikoku: *Bulletin of the Imperial Geological Survey of Japan*, vol. 22, No. 1 (In Japanese)]. Recently, T. Kamiyama and Y. Horikoshi noticed this fact again and applied it to the prospecting and developing of the ore bodies (Collins,

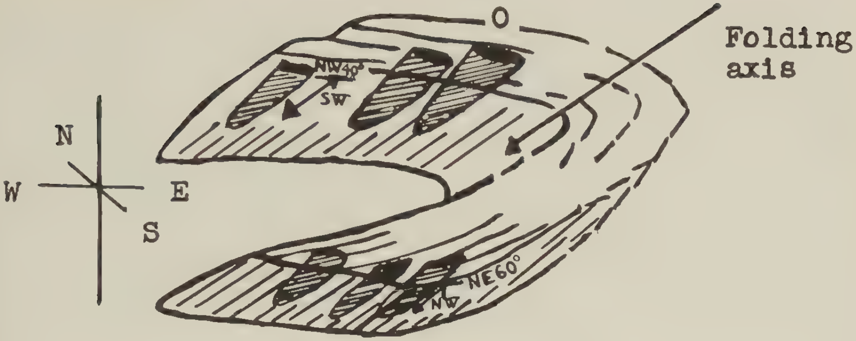

FIG. 2. The relation between lineation, folding axis and shoot of ore body near the Izushi mine (After Y. Horikoshi). O, ore body.

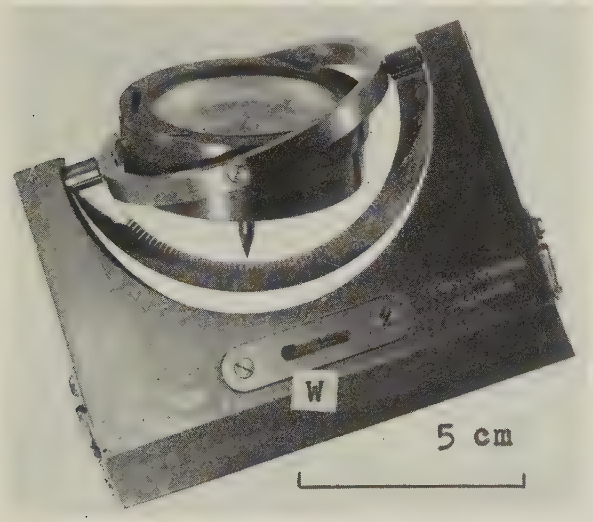

FIG. 3. Universal compass. W, water level.

In 1946, the writer drew the graph for the determination of linear schistosity which is very similar to Ingerson's.[6]

J. J.; A summary of Horikoshi's structure of cupriferous pyrite in schist: *Econ. Geol.*, **45,** 480–481 (1950).

[6] Ingerson and Tuttle had already prepared the graph in 1943, as stated above. But the writer did not know of their publication. Correspondence was impossible until just after the war.

Imai, H., and Kato, Y., On the direction of the lineation in crystalline schist: *Mineralogy and Geology*. **1,** 245–247 (1947) (In Japanese).

In 1948, Professor Nishio[7] of our department devised a compass similar to Ingerson's and made it in his laboratory (Fig. 3). Ten instruments were made there and then about fifty have been manufactured in Katsushima Seisaku-sho (Katsushima Factory).[8] The price of it is $8 to $10. It is used by Japanese geologists in universities, the Geological survey and mining companies. They say that it is convenient not only for the determination of direction of lineation but also of flow structure in igneous rocks and slicken grooves in fault planes.

The writer is indebted to Dr. Ingerson for his kindness in recommending that he prepare this paper and in reading the manuscript.

LEAD CONTAMINATION IN DUCO CEMENT

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Because of its availability and adaptability, Duco cement has become widely employed as a binding agent in powder x-ray work in the United States. Recently investigators (e.g., G. T. Faust, *Am. Mineral.*, **36**, 813, 1951) have observed that Duco gives a broad, diffuse but characteristic band on powder photographs. This contamination is of minor importance and normally does not jeopardize accurate interpretation.

In the course of powder work on fine-grained micas, several x-ray photographs revealed mica lines of unusual intensities, as well as extraneous lines, which made accurate crystal structure determination impossible. At first these photographs were put aside in the belief that they were obtained from micas with a hitherto unreported structure. After several such photographs had accumulated out of a total of 50, some type of contamination was suspected. However investigation showed that the mica samples themselves were pure and therefore that the contamination was introduced during or after the preparation of the mount.

When the Duco was studied microscopically, small black specks, occasionally in considerable quantities, were observed in it as it emerged from the nozzle. These specks were isolated, and a powder photograph of them showed the pattern of native lead. Subsequently, after subtracting the lead lines the structures recorded on the contaminated photographs could be assigned to known mica polymorphs.

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[7] At that time, journals of the United States of America were very sparsely distributed in Japan. Nishio was not aware of Ingerson's paper.

Nishio, S., Measurement of linear schistosity in crystalline schists: *Mining Geology and Applied Geophysics*, compiled by H. Sano. 1951 (In Japanese).

This apparatus has a water-level, as shown in Fig. 3, so we can also determine the dip and strike of the schistosity plane or of bedding plane by using it.

[8] Katsushima Seisaku-sho, 17, 2 chome, Nippori-machi, Arakawa-ku, Tokyo, Japan.

It would seem advisable, therefore, that whenever Duco cement is used as a binding agent in powder work, certain precautions against lead contamination should be practiced. Every time the screw eye is inserted or withdrawn from the tube nozzle, small lead shavings are loosened and are ejected with the cement. Inasmuch as most of the lead shavings usually are expelled with the first emission, the contamination may be materially reduced by discarding the first few drops immediately preceding each use. A more satisfactory method is to slit the tube down the side and empty its contents into an applicator bottle, from which largely uncontaminated cement may be easily withdrawn.

The duPont Company has stated (written communication dated March 26, 1952) that they are currently experimenting with an aluminum type tube which may eventually replace the lead tube now is use. Nevertheless, even with aluminum, this particular problem will still be present. An alternative mounting method which avoids an internal binder altogether may be advisable in some types of work. A procedure which makes use of plastic capillary tubes (K. E. Beu, *Rev. Sci. Instr.*, **22,** 62, 1951) for this purpose has been perfected.

PREFERRED ORIENTATION OF OLIVINE CRYSTALS IN TROCTOLITE OF THE WICHITA MOUNTAINS, OKLAHOMA

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The Wichita Mountains of Southwest Oklahoma are made up of pre-Cambrian igneous rocks, mostly gabbros, anorthosite and granites, which probably form sheet-like intrusions. Troctolites occurring in the oldest intrusion crop out near Roosevelt and other locations of the central Wichita Mountains. The rock has an average composition of 68 per cent bytownite (An_{72-78}), 30 per cent olivine and 2 per cent accessory minerals. It is interpreted as formed by gravity settling of crystals as some outcrops show a downward gradation from an anorthosite through an olivine gabbro to a troctolite.

The troctolite is medium to coarse-grained with feldspar tablets as much as 5 cm. in length and 3 cm. in width, and with olivine crystals as large as 4 cm. in diameter. The average size of grains is about 3 mm. by 2 mm. Some phases show mafic minerals which form interstitial grains between blocky plagioclase crystals while others, generally medium-grained and relatively high in olivine crystals, are markedly saccharoidal. Most of the olivine is evenly distributed in the rock, but local concentration is common. The mineral is altered commonly to goethite, which stands out on the surface of the outcrop. Marked irregularities in grain size, some zonal arrangement of minerals in the coarse-grained phases, and the occurrence of massive mafic minerals suggest that at least a part of the excessively coarse-grained material is pegmatoid in character.

Some troctolites are massive, whereas others show conspicuous banding, which feature in the associated gabbro-anorthosite was interpreted as due to magmatic flow by Walper (3). As the intrusion is a horizontal sheet, the general attitude of the banding of the troctolite is horizontal.

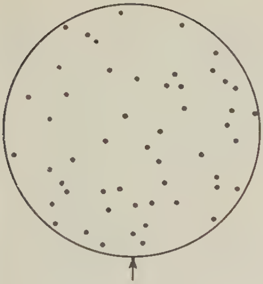
Locally well defined platy and linear parallelism of feldspar in the plane of the banding was observed in several horizons. The bands, usually a few centimeters in thickness, continue with regularity for several yards before they terminate by lensing, or are displaced by small shears. The contacts between adjacent bands are sharp in some cases and gradational in others. Within many of the bands there is a variation from an olivine-rich facies at the bottom to a feldspar-rich one at the top. Repetitions of this feature are common and reversals were observed.

Fabric diagrams were prepared for the olivine crystals from a number of selected specimens of the troctolite. For each slide, the X, Y and Z directions of 52 olivine grains measured in several traverses have been plotted. This number is sufficient to demonstrate the essential features of preferred orientation.

1. *Fabrics of olivine crystals resulting from gravity settling.* The orientation of 52 olivine grains in the troctolite taken from an outcrop one and one-half miles northeast of Roosevelt was analyzed. The fabric of this aggregate of olivine grains was produced by gravitative settling and was not affected by subsequent deformation. The mineral makes up about 28 per cent of the thin section and has the form of equant grains averaging 0.8 mm. in diameter. The resulting diagrams fail to reveal any trace of preferred orientation of olivine (Figs. 1, 2 and 3).

In his analysis of preferred orientation of olivine crystals in peridotites, Turner (2) concluded that the gravitative settling of olivine crystals from basic magmas under static conditions fails to produce preferred orientation of the mineral concerned; this conclusion is borne out by the present study.

2. *Fabrics of the banded troctolite.* Two selected troctolites with banded



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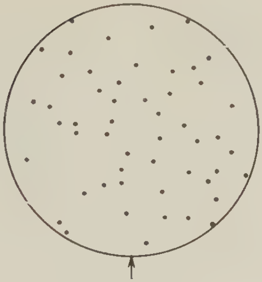

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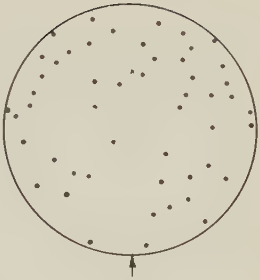

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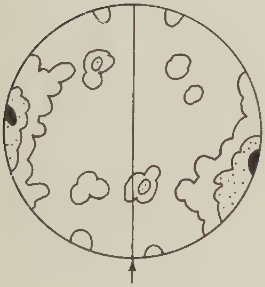

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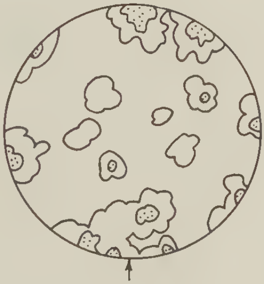

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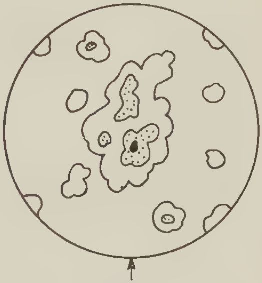

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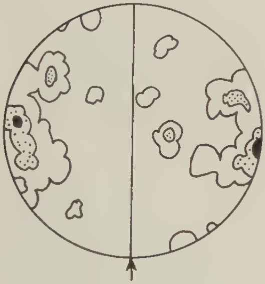

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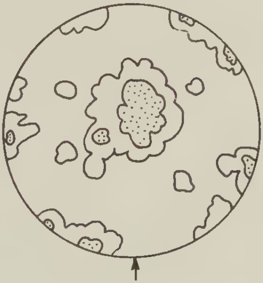

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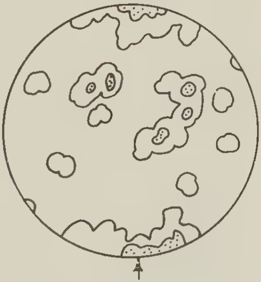

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FIGS. 1–3. Orientation of X, Y and Z respectively in 52 olivine grains in troctolite, H-25. Location: one and one-half miles northeast of Roosevelt (SW $\frac{1}{4}$, SW $\frac{1}{4}$, Sec. 33, T. 5 N., R. 17 W.).

FIGS. 4–6. Orientation of X, Y and Z respectively in 52 olivine grains in banded troctolite, H-41; contours, 6-4-2 per cent. Location: 13 miles southeast of Roosevelt (NE $\frac{1}{4}$, Sec. 9, T. 3 N., R. 15 W.).

FIGS. 7–9. Orientation of X, Y and Z respectively in 52 olivine grains in banded troctolite, H-47; contours, 6-4-2 per cent. Location: 14 miles southeast of Roosevelt (SE $\frac{1}{4}$, SE $\frac{1}{4}$, Sec. 5. T. 3 N., R. 15 W.).

structure were analyzed. The olivine grains are xenomorphic, with some having a weak undulose extinction. Many of the olivine grains are slightly but distinctly elongated parallel to the banding of the rock.

In Figs. 4, 5 and 6 are plotted the X, Y and Z directions measured in 52 olivine grains from one section of the typical banded troctolite collected from an outcrop 13 miles southeast of Roosevelt. The vertical line of Fig. 4 indicates the section parallel to the trends of bands, and it is seen readily that there is a distinct preferred orientation of X with a maximum at right angles to the plane of banding. In Fig. 6 the preferred orientation of Z direction within the plane of banding is distinct. In Fig. 5, Y shows a less obvious tendency to preferred orientation within the plane of banding and perpendicular to Z.

Figures 7, 8 and 9 illustrate the orientation of olivine crystals in the banded troctolite taken from an outcrop 14 miles southeast of Roosevelt. These diagrams, like Figs. 4, 5 and 6, show fairly distinct maxima for X, Y and Z in mutually perpendicular directions. Again the X maximum, almost normal to the banding, is the most conspicuous.

The preferred orientation patterns for olivine of flow-banded troctolites (Figs. 4–9) are reminiscent of those recorded by Phillips (1) and by Turner for olivine of banded or schistose peridotites which appear to have been emplaced by flow of a lubricated mass of crystals or by deformation subsequent to intrusion. Phillips refers to similar observations by Andreatta for olivine of olivinite and by Ernst for olivine of olivine-schist of metamorphic derivatives.

The conclusion of this study is that in the Wichita Mountains olivine of non-banded troctolites, the crystals of which were concentrated by gravitative settling, show no preferred orientation; whereas olivine of flow-banded troctolites shows marked preferred orientation with Y and Z in the plane of banding.

References

1. Phillips, F. C. (1938), Mineral orientation in some olivine-rich rocks from Rum and Skye: *Geol. Mag.*, **75**, 130–138.
2. Turner, F. J. (1943), Preferred orientation of olivine crystals in peridotites, with special reference to New Zealand examples: *Trans. Royal Soc. of New Zealand*, **72**, pt. 3, 280–300.
3. Walper, J. L. (1951), Assimilation in the Cold Springs Area of the Wichita Mountains Igneous Complex, Oklahoma: *Am. Jour. Sci.*, **249**, 47–65.

The University of Toledo and three Toledo glass companies have announced the establishment of a Graduate Institute in Silicate Chemistry and Related Sciences. The initial sponsors are the Libbey-Owens-Ford Glass Co., Owens-Illinois Glass Co., Owens-Corning Fiberglas Corporation, and the University. Heading the institute as director and also serving as professor of silicate chemistry will be Dr. Wilhelm Eitel, who was engaged at the Office of Naval Research in the synthesis of silicate minerals. For a period of twenty-five years Dr. Eitel organized and directed the Kaiser Wilhelm Institute of Silicate Research in Berlin-Dahlem, Germany.

SELECTED NOTES FROM NEWS LETTER, AMERICAN GEOLOGICAL INSTITUTE

David M. Delo, who has served as Executive Director of the American Geological Institute since it began operations on June 1, 1949, has resigned, effective in July to accept the presidency of Wagner College, Staten Island, New York. A new Executive Director will be appointed in the near future and Institute activities will continue without interruption.

The first printing of 5,000 copies of the preliminary career booklet entitled, "Shall I Study Geological Science?" has been exhausted. A second printing of 5,000 is now available for distribution. The booklets may be secured without charge by individuals, departments or societies if they will contact A.G.I. Headquarters: 2101 Constitution Ave., Washington, D. C.

The sale of A.G.I Report No. 6, "Departments of Geological Science in Educational Institutions of the U. S. and Canada" has been better than anticipated. Only about 100 copies of the original printing are still in stock. Those desiring the Directory should therefor order immediately. Price $1.00 from A.G.I. Headquarters.

Plans for bi-monthly issuance of a compilation of current geological and geophysical abstracts are now in the making. The publication will include authors abstracts from the geological journals in the U. S. and Canada, state and federal reports, and other publications whenever possible. These will be photolithed and issued in inexpensive form, with a current and annual index.

The new "compilation" should be invaluable to industrial geologists who do not have a large library available and to others desiring to keep abreast of current publications at a small expenditure of time and money.

Distribution will be through annual subscription. In accordance with A.G.I. policy, the "compilation" will be made available at the lowest feasible cost.

48th MEETING, CORDILLERAN SECTION, G.S.A.

"More than 650 geologists, paleontologists, seismologists and hydrologists attended the 48th meeting of the Cordilleran Section, G.S.A. held under the sponsorship of the Arizona Geological Society at the University of Arizona, April 10–14. About 375 attended the various field trips, including about 130 on the two-day trip from Tucson through the Ray-Globe-Miami mining district, and on to Holbrook. This trip traversed Arizona from the basin-range type of country around Tucson, across the mountainous district separating the desert from the Colorado Plateau and on to the South Rim of the Plateau.

"The Guidebook prepared in connection with the field trips contains 150, $8\frac{1}{2}\times 11$ pages, 51 figures and 5 tables. The figures include 19 photographs, 17 maps and 15 sections. It is the only currently available comprehensive publication on the geology of southern Arizona. In addition to the detailed road logs there are 15 articles dealing with the geology of the area. Price, $3.50: remittance should accompany orders."

New Section Officers for 1952–1953 are:

Chairman—William C. Putnam, University of California at Los Angeles.
Vice-Chairman—M. Y. Williams, University of British Columbia, Vancouver, B. C.
Secretary—V. L. VanderHoof (reelected for a third term) Independent Exploration Co., Santa Barbara, Calif.

The retiring officers of the Cordilleran Section are:

Chairman—Ian Campbell, C.I.T., Pasadena, California.
Vice-Chairman—C. M. Gilbert, University of California at Berkeley.
Secretary—V. L. VanderHoof.

Professor Emeritus Charles Palache, whose address has for many years been at 106 Appleton St., Cambridge, Massachusetts, desires to inform his friends and correspondents that after Sept. 10, 1952 his address will be changed to Charlottesville, Virginia, *R.F.D.* 3, Box 205-D.

His home will be on the property of Charles O. Gregory of the Law School of the University of Virginia. This lies in the suburban subdivision of Bellair, about one mile west of the University on Route 250 from Charlottesville.

Mr. Palache will still receive mail addressed to Harvard University, Department of Mineralogy and Petrography, Geological Museum, Oxford Street, Cambridge 38, Massachusetts.

FURTHER NOTE ON UNIT CELL AND SPACE GROUP OF GLAUCOCHROITE

J. H. O'MARA, *Carter Oil Co., Box 209, Miles City, Montana*

Through the courtesy of Dr. Wilhelm Eitel, Electrotechnical Laboratory, Norris, Tennessee, I have become aware of a prior study of the unit cell and space group of glaucochroite by H. O'Daniel and L. Tscheischwili included in their more detailed paper, "Strukturuntersuchungen an Tephroit Mn_2SiO_4, Glaukochroit $(Mn, Ca)_2SiO_4$, und Willemit Zn_2SiO_4 von Franklin Furnace," *Zeit. Krist.*, (A), **105,** (1943), pp. 273–278. Issues of *Zeitschrift für Kristallographie* for the period covered by World War II were unavailable in the library consulted (Harvard University) at the time my short article was published in *Am. Mineral.*, **36,** 918 (1951). However, the data are in reasonable accord with the earlier published ones.

The Secretary of the Mineralogical Society of America has been requested by the Tolstoy Foundation to aid a certain Mrs. Maria Chijikov to locate her son, Mr. George Chijikov-Roman. There is little information about him except that he worked in a museum in the field of Mineralogy. If any one has information about him, please contact the Tolstoy Foundation, Inc., Search Department, 300 West 58th Street, New York, N. Y.

TENTH ANNUAL PITTSBURGH DIFFRACTION CONFERENCE

Preliminary Announcement

The Tenth Annual Pittsburgh Diffraction Conference will be held at Mellon Institute of Industrial Research, Pittsburgh 13, Pa., on November 6 and 7, 1952. Technical sessions are being arranged on *Instrumentation and Methods*, *Neutron Diffraction and General Diffraction Studies*. Contributed papers on these and related subjects will be considered in the order in which they are received. Titles should be submitted to the Program Chairman, Mr. R. K. Scott, Hall Laboratories Inc., Box 1346, Pittsburgh 30, Pa., before September 1, 1952.

This year's conference will include a symposium of invited papers in the field of *Order—Disorder Studies.*

For further information, and for a copy of the preliminary program when available, write to Mr. E. E. Wicker, U. S. Steel Company, Research and Development Laboratory, 234 Atwood Street, Pittsburgh 13, Pa.

BOOK REVIEWS

SPECTROCHEMICAL ANALYSIS, BY L. H. AHRENS, 364 pp., Cambridge, Mass., Addison-Wesley Press, Inc., 1950.

WAVELENGTH TABLES OF SENSITIVE LINES, BY L. H. AHRENS, 92 pp., Cambridge, Mass., Addison-Wesley Press, Inc., 1951.

Spectrochemical analysis of natural materials is still largely an art despite the fact that great progress has been made in the past 10 years in making such analysis reproducible from laboratory to laboratory. In preparing the two volumes here reviewed, Professor Ahrens, one of the leading American practitioners of the spectrochemical art, has performed a great service to those engaged in making spectrochemical analyses and to those who use them.

Professor George R. Harrison, in his foreword to the first volume, states well the need for the book:

> Several excellent books which deal with the basic theory and application of spectroscopy to the analysis of materials have appeared recently, but there has been great need for a series of volumes dealing more specifically with the detailed problems that arise in analyzing samples of one given type or another. The present volume will go far toward meeting this need insofar as the mineralogist and the metallurgist are concerned; after discussing spectrochemical analysis briefly it concentrates on the special problems met with in analyzing rock, ore, mineral, and soil samples, and conveniently integrates the accumulation of new lore for which a vast and rapidly growing literature must otherwise be combed.

In his preface, Professor Ahrens sets forth the scope of the book:

> In recent years spectrochemical analysis has been effectively employed to an ever-increasing extent for the analysis of a very wide variety of materials. Included in this list are minerals, rocks, soils, ceramic materials, refractories, slag, and biological ash. . . . There exists an urgent need for books on the analysis of the various substances which have been noted above and this book has been written in the hope that it will partly fulfill this need. It has been prepared chiefly for the analysis of minerals, rocks, and soils, but much of its content applies also to the analysis of ceramic materials, refractories, slag, and biological ash. . . .
>
> The source of excitation that has been most extensively employed for the analysis of minerals, rocks, soils, and related material is the d.c. arc, and this book restricts itself to the use of this source. . . .
>
> This book has been divided into two sections. The first, based partly on a course in spectrochemical analysis given by the author in the Department of Geology at the Massachusetts Institute of Technology, covers theory, general principles, techniques of analysis, and other pertinent aspects of spectrochemical analysis. In the second section the *spectrochemistry* of each element is discussed. *Instrumentation has in the main been omitted from this book.* Most necessary information of this type (description and discussion of spectrographic equipment) may be found in some of the general texts listed in the bibliography.

Part I, General Principles, consists of 10 chapters, covering Introductory Remarks, The Origin and Interpretation of Spectra, Some Physical Features of the D.C. Arc Discharge, Power of the Arc Source, Qualitative Analysis, Selective Volatilization, General Principles of Quantitative Analysis, Effect of a Change of Composition on Line Intensity, The Photographic Measurement of Radiant Energy and the Construction of a Working

Curve, and the Emission of Band Spectra from the Arc. There is a wealth of material in these chapters thoughtfully and authoritatively discussed, such as, for example, arc temperatures, electrode shapes and sizes, compositional effect in qualitative analysis, and the very important subject of sampling and preparation of specimens. The discussion of this last subject is restricted to methods of sampling and preparing material received in the laboratory. The larger question of sampling in the field for spectrochemical analysis perhaps has no place in this book; but it is a subject badly neglected and one needing more research and discussion than it is currently receiving.

Part II, The Elements, consists of 13 chapters containing discussions of general semiquantitative and quantitative methods applicable to a large number of elements and to appropriate groups of elements. The information in these chapters is detailed and will be found of inestimable practical help to those engaged in the analytical procedures. Of particular interest is the discussion in chapter 23, Common Elements Usually Present as Major Constituents (Si, Al, Ca, Mg, Fe, Mn, Ti, K, and Na).

The book concludes with an extensive but selective bibliography, an adequate author index and general index, wavelength tables, and the periodic table of elements. The wavelength tables, a notable feature of the book, are the basis of the second volume here reviewed.

This second volume, Wavelength Tables, gives in tabular form "the most sensitive lines of the elements in the arc and possible interfering lines within ±0.4–0.5 Å of each sensitive line. Prepared particularly for the analysis of minerals, rocks, soils, meteorites, and related materials." Information is given for 68 elements and includes general comments on line sensitivity, line interference, excitation potentials, and a table showing the detection-limit concentrations of the elements in the d-c arc. There is also a separate table showing the most sensitive lines of the rare-earth elements and a table showing line sensitivities for visual (spectroscopic) analysis. Revisionary data on the well-known M.I.T. wavelength tables are included, together with some line coincidence data and a bibliography.

The wavelength tables constituting the body of the work are arranged alphabetically by elements. A most notable feature of the tables is the listing of interfering lines.

The two volumes have substantial bindings, pleasing formats, and are printed on non-glare paper. The second volume, Wavelength Tables, is printed on a gray paper that is particularly pleasing to the eye, and the tables are easily read.

These two books can be heartily recommended to spectroscopists, geologists, geochemists, metallurgists, soil scientists, and all others who have a use for spectrochemical analyses.

John C. Rabbitt
U. S. Geological Survey, Washington, D. C.

ELEMENTI DI MINERALOGIA, by Paolo Gallitelli, Nistri-Lischi Editori, Pisa, Italy. 1951. xvi and 575 pages, 455 text figures, 14 plates. Price, paper bound, Lire 4,000.

It is extremely interesting to compare, from time to time, the evolution of modern mineralogy as reflected in textbooks. It is with the greatest sympathy that the reviewer follows the efforts of leading teachers of mineralogy and authors of textbooks in order to see how they try to harmonize the requirements of routine instruction in geometric and physical crystallography and of descriptive mineralogy with the principles of basic physical chemistry, structural investigations or geochemistry.

One may have different opinions as to the actual usefulness of the "orthodox" or "conservative" as opposed to the "revolutionary" types of textbooks that have preserved or broken with the traditions of the Berzelius chemical classification or the Dana textbook style. This is especially true if the book is to be designed to attract not only specialists in mineralogy but also students in chemistry, engineering and practical geology. Often the problem has arisen whether or not it is advisable to introduce a chapter on petrology into mineralogical textbooks. Most authors have not, since they were of the opinion that the inclusion of such a chapter would increase the size beyond reasonable limits. The fact remains, however, that most students of mineralogy must combine a fundamental knowledge of rock-forming minerals and of rocks with a good understanding of the basic methods of mineralogical determination by optical techniques or by *x*-ray diffraction. This also holds true for geology students interested in sedimentary rocks.

This dilemma of teaching mineralogy and writing mineralogic textbooks brings about an astonishing number of individual viewpoints. In this respect this book by an outstanding Italian mineralogist is most pleasing, because the techniques of presentation are combined for maximum usefulness to the reader. The author has found it possible to reconcile the "orthodox" and the "revolutionary" approaches due to his wide experience in instructing chiefly students of chemistry and general science at the University of Modena. He emphasizes the need of a good practical knowledge of geometric crystallography, including methods of crystal projection, calculation of the axial elements and projection. In addition the author stresses *x*-ray methods, from the Laue diagram and powder patterns to the rotation and Weissenberg goniometric method, including the application of the Ewald construction, the reciprocal lattice, and the simplified Fourier and Patterson analysis. Equally comprehensive are his discussions in the fields of applied mineralogy. The instruction is even extended to the techniques of examining polished and etched sections in reflected light. The reviewer is pleased to note that a mineralogical author discusses all these items not merely in a few paragraphs but in considerable detail based on his own broad experience. The discussion is not restricted to natural minerals, but is extended to include numerous inorganic crystal structure types, such as alloys, intermetallic compounds, etc. The reviewer does not recall many mineralogic textbooks of a similar size which give their readers an equally impressive introduction into applied mineralogy.

In the physical-chemical discussion of mineral genesis, the origin of magmatic rocks is not outlined in detail, but the importance of the Gibbs phase rule is stressed. Crystallochemical principles in relation to geochemical problems, minerogenesis and mineral stability are likewise emphasized. The application of V. M. Goldschmidt's and L. Pauling's laws of ionic replacement, ionic radii and their ratios, especially of the polarization phenomena are treated in carefully prepared special sections.

In comparison with the 450 pages comprising the general chapters, the 100 pages devoted to "Examples of Special Mineralogy" may appear very inadequate. However, it may be stated that additional information on the most important minerals is found also in paragraphs of the general part. Therefore an evaluation based only on the number of pages devoted to the "examples" does not do full justice to the essential minerals that the author selected. The author came to the conclusion that by far most of his students are interested in the description of ore minerals from which the fundamental metals are obtained (Fe, Al, Cu; Pb, Ag, Zn, Cd, grouped genetically together; Sn, Hg, Au, Pt, Ni, Co, Mn, Cr), and the metals of "modern metallurgy" (Ti, W, V, Ta-Cb, Li, Be, Sb, As, Bi). The "non-metalliferous" minerals including those of Na, K, Mg, B, the nitrates, apatite, those of Ba, Sr, the ornamental stones, fluorite, S, pyrite, graphite, the radioactive minerals, and the rock-forming silicates are discussed in 30 pages, and classified according to Strunz's structural scheme, with the Machatscki type formulation. It is surprising how satisfactory the information given here really is, in such a brief space devoted to "special mineralogy." Of considerable aid are the photographic reproductions of selected minerals which are, with a few exceptions, of excellent quality.

It would be surprising if such a new approach toward writing a mineralogical textbook would not meet with some objections. The generally high level, however, on which the author has made his selections makes evident how carefully be surveyed the modern and classifical international literature of crystallography and physical chemistry. It would be erroneous if the reader would consider it as "elementary" throughout. On the contrary, the reviewer was sometimes surprised to find highly interesting and still unsolved problems discussed. The following may be mentioned as a single example. On page 142 regular intergrowths of quartz and calcite are referred to which E. S. Dana (*Am. J. Sc.*, (3) **12,** 448, 1876; *Zeit. Krist.*, **1,** 39, 1876) described from Specimen Mt., Yellowstone Park, in which $(01\bar{1}2)$ of calcite is intergrown parallel to $[10\bar{1}1]$ of quartz. This rather neglected observation (not cited in Dana's "System of Mineralogy," new edition) is related to the rare twin law of quartz with $(10\bar{1}1)$ as the twinning plane (in the "Reichensteiner Quarzgruppe" described as "Griesental law" by V. Goldschmidt (*Tscherm. Min., Petro. Mitt.*, **24,** 157–166; 174–179, 1905). A re-examination would be highly desirable with an extensive study of the structural conditions for regular intergrowths and the meaning of what Goldschmidt defined as an "induction effect" (Begünstigung) by the calcite as host phase.

It may be regretted, on the other hand, that in the crystallographic-optical chapter (p. 288) the elementary Fresnel construction for the determination of extinction directions in random sections of crystals with low grade of symmetry is not described. This also would have contributed to a better understanding of how the indicatrix is oriented by the universal stage method, which is indispensable for the identification of natural and synthetic crystals. Some doubts might be expressed as to whether an average reader would be able to follow profitably the recommended study (p. 308) of the highly mathematical theory of circular birefringence recorded in the papers of M. Born and B. Y. Oke (*Proc. Roy. Soc. London,* **150,** 84, 1935; **151,** 339, 1936). A quotation from the classical "Lehrbuch der Kristalloptik" by F. Pockels (Leipzig, 1906, especially pp. 307 to 335) with a short discussion of V. von Lang's double-shelled wave surface would probably have sufficed. In the chapter on the optical examination of opaque minerals (pp. 314–318) a reference to the excellent paper of M. Berek (*Fort. Min.*, **22,** 1–104, 1937), especially on the photometric methods for the determination of the orientation of the absorption indicatrix, seems necessary. Special mention should be made of the prevailingly excellent crystallographic illustrations, especially in the chapter on crystal growth and twinning (pp. 125–144).

The reviewer has discovered certain minor defects in the text such as erroneous names of authors and localities which can be remedied in a future edition. Also a few additional suggestions may be added. In the discussion of the symmetry and space groups (pp. 58, 168) the symbols and deductions of A. Schoenflies are used exclusively. The reviewer is of the opinion that the internationally adopted Mauguin-Herrmann symbols must also be used in modern structure discussions.

In the special part, on page 477, speaking of stannite, associated with cassiterite, the important mining locality of Llallagua is not mentioned. This would have offered a good opportunity to call attention to the highly instructive occurrence of cassiterite formed from gel minerals by the decomposition of sulfo-stannates in the oxidation zone of the deposits.

Somewhat surprising, at least for an American reader, is the omission of kernite which is by far the most important boron mineral on the American continent. On page 535, the polymorphism of $CaSiO_3$ is not mentioned, although the occurrence of the complex group $[Si_3O_9]$ as a structural unit is referred to. Pseudo-wollastonite is a typical devitrification product in window glass melts.

Surprisingly short is the discussion of the clay minerals which are briefly characterized on page 219, and Fig. 300, as having the H_2O interlayer structure of vermiculite (Hendricks), but only kaolinite is given a few general remarks. Halloysite, montmorillonite, nontronite, and the hydromicas (illite, etc.) are either referred to very briefly or omitted. This can not do justice to the great importance of these minerals in sedimentary mineralogy and soil formation, not to speak of their importance in fuller's earth (e.g. fibrous attapulgite) or as catalysts for low-temperature organic syntheses, etc.

These few selected criticisms are offered as suggestions in the revision of the book in forthcoming editions. The Italian mineralogists can in all events feel very happy to see this fine book given a position of merit in international mineralogical literature.

Wilhelm Eitel,
University of Toledo, Toledo, Ohio

CHEMISCHE ANALYSE DER GESTEINE UND SILIKATISCHEN MINERALIEN

by J. Jakob, Verlag Birkhäuser, Basel, 1952. Clothbound, 180 pages. Price 18.70 Fr. for bound copy.

This is Volume VII, chemical series, of Lehrbücher und Monographien aus dem Gebiete der exakten Wissenschaften. The book is divided into two parts: the first and larger portion deals with the methods generally applicable in the analysis of silicate rocks; the second part outlines specific applications and modifications for the analysis of minerals such as albite, anorthite, beryl, biotite, hornblende, muscovite, etc.

The procedures are clearly written and are in general agreement with those given in standard texts such as Hillebrand's Bulletin 700 published by the U. S. Geological Survey. The presentation reflects the attitude of a good professor in his classroom. Usually a paragraph on general considerations opens the discussion, then follow in logical order a brief outline of the principles of the method and finally the exact directions for an analysis. Procedures are outlined for the determination of both the major and minor constituents of silicate rocks. Very few references and supporting data are given. However, the existence of tri- and quadrivalent titanium in certain minerals has been demonstrated.

The absence of a subject index somewhat detracts from the usefulness of the book, but this omission is partly excusable because it is a short book and contains a fairly complete table of contents.

James I. Hoffman,
National Bureau of Standards, Washington 25, D. C.

THE BARKER INDEX OF CRYSTALS: A METHOD FOR THE IDENTIFICATION OF CRYSTALLINE SUBSTANCES,

by M. W. Porter and R. C. Spiller. Volume 1, Tetragonal, Hexagonal, Trigonal, and Orthorhombic Systems. Part 1, Introduction and Tables, x+250 pp., 74 figures. Part 2, Crystal Descriptions, x+1,027 pp. Cambridge. W. Heffer and Sons, Ltd., 1951. Prices. Part 1 30s; Part 2 £4 10s. Part 1 and 2, £6.

This volume, which is an index to most of the known tetragonal, hexagonal and trigonal, and orthorhombic substances, is essentially a treatise on determinative morphological crystallography as initiated by Dr. T. V. Barker, who died in 1931. It is an attempt to set down rules for dealing with crystal geometry "which will enable two independent crystallographers who have measured crystals of the same substance to choose the same set of angles for identification" and, thus, to quickly and easily identify the substance by its crystallography. The rules were formulated by Barker and have been applied by the authors and others to the substances given in Groth's *Chemische Krystallographie* and in a few other sources.

The statement of rules governing the choice of unit form (setting) and orientation is lucid and straightforward. The unit plane which is selected is that which gives the greatest number of simple planes, these being {001}, {100}, {010}, {110}, {101}, {011}, and {111}. In the hexagonal system 4-index symbols, 2 may enter into the indices of simplest planes. In cases where two or more different unit planes give the same number of simple planes, rules are set forth to eliminate all except one. Since the method is concerned with the identification of substances by their crystal form, it may not be too important that the unit thus chosen can conceivably differ from the structural unit. The effects of glide planes, screw axes, and lattice centering upon the occurrence of simple planes is ignored; but oftentimes the selection of a unit which gives the largest number of simple planes does yield the structural unit, so the disadvantage is not too serious.

An elementary explanation of the Barker Index for non-crystallographers by L. W. Codd introduces Part 1 of Volume I. This treatment is fairly rigorous and probably useful to beginning students of geometrical crystallography. It discusses: interfacial angles; spherical, stereographic, and gnomonic projections (the spherical projections which he uses are not too spherical--but serve their purpose very well); and zonal relationships. A heavy emphasis on zones seems to spring from a reluctance to leave one-circle goniometry, the principal argument being the advantage of being able to identify symmetries (highly doubtful!). Since one setting for many crystals is frequently all that can be made, zones and zonal relationships are actually better studied by measuring on a two-circle goniometer and plotting on a Wulff stereographic net.

Aside from the fact that there probably can be no short cut to an understanding of crystallography, such as Mr. Codd attempts, several non rigorous approaches leave much to be desired. For example, he shows the determination of zone symbols by the usual cross multiplication of indices of two faces in the zone, but in the cross multiplication he uses as indices of the two faces *hkl* and *pqr*. This should prove rather confusing to the beginner. The indexing of faces by use of the stereographic projection is not at all convincing. Too often the word *setting*, meaning unit, is ambiguously used to refer to orientation or to unit and orientation. It would be less confusing to restrict *setting* to the position of mounting of a crystal for measurement and to use the rigorous terms *unit* and *orientation* where they apply. Dr. Hey, in his later treatment, has been more precise in his use of *setting*. On page 78, however, he uses *setting* in the sense of *unit*, but in Part 2, page viii, *setting* carries the connotation of combined *unit* and *orientation*.

Codd describes seven crystal systems, but he follows the British custom of recognizing a trigonal system which contains seven crystal classes, of which two must be hexagonal while the other five may be hexagonal or rhombohedral. Hey recognizes this ambiguity, but uses the *trigonal system* in spite of its non rigorous character.

Pages 68 to 119 of Part 1 are AN INTRODUCTION TO THE BARKER INDEX by Dr. M. H. Hey. His writing is very clear, rigorous, and in fine style. This section makes no pretense of being an introduction to goniometry, but it would certainly be of considerable value to the beginner in crystallography. He emphasizes that the Barker Index reduces the 32 crystal classes to 11 centrosymmetric Laue groups by assuming the existence of a center of symmetry in all cases. In the tegragonal, hexagonal, and trigonal systems he notes the existence of *restricted* and *free* Laue groups based upon the presence or absence, respectively, of vertical planes of symmetry. In the *restricted* classes the choice of orientation is fixed, but there is freedom of choice of orientation in the free classes. Hey states that *orientation problems only arise in the orthorhombic, monoclinic, and anorthic systems*, but his *free* classes present some problems as well.

The critical angle for orthorhombic, tetragonal, hexagonal and trigonal substances in the Barker Index is the angle *cr* ($001\wedge 101$). In the orthorhombic system there are two additional angles. The first, *am* ($100\wedge 110$), must be less than 45° but closer to 45° than *cr* or the third angle *bq* ($010\wedge 011$). These angles are in cyclic order. In case the angles cannot be measured because a plane or planes are missing, they may be calculated according to given procedures or by methods which are available to any crystallographer. Isometric substances are not included in the Index, since they do not have distinctive angles.

Once the classification angle or angles are known, it is a simple matter to refer to the determinative tables where *cr* values are listed according to increasing magnitude. The subsidiary angles and, or the physical properties are then sufficient to narrow the choice from the range of possibilities to the correct species.

Hey has done a real service in his excellent treatment of *goniometry under the microscope and from photographs.*

The experienced crystallographer will be able to proceed with the Index with not more than a half hour study. He will find useful the *multiple tangent* tables; the *determinative geometrical* tables based on increasing angle *cr;* the *determinative optical* tables where uniaxial substances are listed according to increasing ω and orthorhombic substances are listed according to increasing β (beta is improperly called the ('mean') index in one section); and the determinative tables based on *increasing specific gravity* and on *increasing melting points.* The Alphabetical List of English Chemical and Mineralogical Names, plus the Alphabetical List of German Chemical Names as Used by Groth complete Part 1. All of these tables and lists are cross indexed with the thorough summaries of the properties of the substances, which are given in Part 2.

Part 2 is composed of three different sections devoted to tetragonal, hexagonal and trigonal, and orthorhombic substances. Within each section the substances are listed in the order given by Groth. Each substance is named and chemically defined and is given a reference number (there are 401 tetragonal, 434 hexagonal and trigonal, and 2,156 orthorhombic entries). References to Groth and other chemical works are made. The classification angles are listed, and the transformation formula—Barker to Groth—is given. Critical crystal forms are noted; the form indices are based on the Barker unit and orientation; the form letters are those of Groth for cross reference purposes.

A condensed description of the substance as given by Groth follows. (Ambiguity arises here, however, for the form indices are not those of Barker but of Groth.) The crystal class of the substance is given both with Hermann-Mauguin and with Schoenflies symbols. The habit, physical, and optical properties are summarized. Transformation formulae—Groth to Barker and others—are given. The description closes with the *x*-ray spacings where they are known of the three most intense lines as given by *ASTM.*

These two parts of volume 1 represent a prodigious amount of work on the part of the disciples of Barker's approach to determinative crystal geometry. That other approaches might serve as well is of little moment. The fact is that through this work the authors have raised geometrical crystallography from the realm of the abstract to a position of unique value as a determinative tool. No longer can crystallography be considered an adjunct of mineralogy, alone. This work must go a long way toward convincing the chemical profession and others that crystallography is a tool without which they cannot afford to continue. The mineralogist may find Part 1 of this volume sufficient for determinative purposes, since the *New Dana System of Mineralogy,* Volume I and II, supply most of the information that is in Part 2. It would seem, however, that the cross references involved in Parts 1 and 2 would make the purchase of both highly desirable.

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PRINCIPLES OF GEOCHEMISTRY by Brian Mason, 276 pp., 42 figures, 39 tables. John Wiley and Sons, Inc. 1952. $5.00.

Here at last is the book that fulfills adequately the long-felt need for a *textbook* in geochemistry, written by a student of one of the pioneers and outstanding figures in the field, V. M. Goldschmidt. Although another recent book, *Geochemistry* by Rankama and Sahama, is more encyclopedic in scope and offers more detailed information on the occurrence and distribution of the individual elements, *Principles of Geochemistry* by Brian Mason of Indiana University, reaches the happy intermediate level, considerably above that of an elementary treatise and somewhat below that of a source book. Not only has the author succeeded in distilling down the enormous vatfull of geochemical data available from the literature, but he has likewise been able to instill in his product a flavor that will undoubtedly be palatable to the majority of users.

The plan of the work has obviously been carefully fashioned. After a short introduction dealing with definition, history and references, Chapter two discusses the relations of the earth to the universe. Here are assembled brief accounts of the most recent ideas on the nature, age and origin of the universe, nature and origin of the solar system (emphasizing the version of von Weizsäcker), the compositions of the universe, sun, planets and meteorites, and finally, cosmic abundance and origin of the elements.

The structure and composition of the earth are the subjects of Chapter three, in which seismic, density and temperature data are reviewed, structural conclusions summarized, various earth models are critically examined and the zones of the earth—atmosphere, biosphere, hydrosphere, crust, mantle and core are chemically described. The chapter concludes with sections on the primary geochemical differentiation of the earth, geochemical classification of the elements and an interesting and well-constructed bit on the pre-geological history of the earth.

Chapter four, Some thermodynamics and crystal chemistry, is in part a diversion from the general theme of the book. Most of it is chemistry and basic crystallography which the author deems necessary for a complete understanding of geochemical concepts. If the book is used as a text, this section may be of value to students whose backgrounds in collateral fields is incomplete. Magmatism and igneous rocks, Chapter five, considers the nature and composition of magmas, the crystal chemistry of the common rock minerals, crystallization of silicate melts, their minor and volatile elements and the relation between ore deposition and the magmatic cycle. It is interesting to speculate why the author, in choosing his species lists of the groups of common minerals, included such a rare example as johannsenite under the pyroxenes and omitted the more widespread hastingsite under amphiboles. In some groups the relations between "species" are not clearly indicated nor the complete isomorphism in series indicated. The discussion of pegmatites, when one considers the wealth of recent literature, is elementary, and it is most unfortunate that the author assists in perpetuating the notion that some mineralogically simple pegmatites have formed by differential fusion.

Sedimentation and sedimentary rocks are treated in Chapter six under such subtopics as composition, physico-chemical factors, pH, redox potential, colloids and products of sedimentation. Next follow three chapters (7, 8, 9) describing successively the hydrosphere, atmosphere and biosphere, each as to nature and composition and development. In the last of the three are sections on coal and petroleum as well as trace elements in biogenic deposits.

In Chapter ten, on Metamorphism and metamorphic rocks, the author considers chemical and mineral composition, mineral stability, thermodynamics and kinetics of metamorphism, metamorphic phase rule, facies, metasomatism and ultra metamorphism. It is gratifying to note that the author deemphasizes the role of ionic migration through solids as an important factor in large-scale rock transformations. The final chapter, The geochemical cycle, is a succinct summation.

Minor typographical and grammatical defects are at a minimum and there appear to be few significant omissions or misstatements. The organization is coherent, the presentation is cogent and the topography is clear. Line drawings are completely legible, but their number probably could have been increased. Each chapter is followed by an excellent selected bibliography which includes " . . . comprehensive texts, significant recent papers (especially those in journals not usually referred to by geologists), and review articles with comprehensive bibliographies." Fortunately Russian sources have not been neglected, and the reviewer was pleased to note a description, one of the few in English, of Vernadsky's terms, clarke and concentration clarke (pp. 42–43).

To all students of geochemistry, whether their interest stems from the preficial or the sufficial roots of the name, this book is completely recommended as a highly readable and useable integrated account of the physical and chemical history of our planet.

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REPORT OF THE COMMITTEE ON THE MEASUREMENT OF GEOLOGIC TIME, 1950–51. Division of Geology and Geography, National Academy of Sciences—National Research Council. Publication 212, 140 pp., 1952. Mimeographed, $1.00.

The 1950–51 report of the Committee on the Measurement of Geologic Time, prepared under the direction of John P. Marble, Chairman, includes the following reports: (1) Summary report of the Committee on the Measurement of Geologic Time for 1950–51 by J. P. Marble; (2) Annotated Bibliography of Articles Related to the Measurement of Geologic Time, compiled by J. P. Marble (nearly 400 entries); (3) Abstracts of Papers delivered at the Symposium on the Measurement of Geologic Time, *Am. Geophys. Un.*, April 30 and May 2, 1951 (Articles published *in toto Trans. Am. Geophys. Un.* 33(2), 150–203, 1952); (4) Extracts from the Preliminary Report of the Committee on the Measurement of Geological Time in India, 1947–1950; and (5) Natural Variations in Isotopic Ratios of the Chemical Elements (A Report to the Commission on Atomic Weights, International Union of Chemistry, September, 1951) by J. P. Marble.

As in previous years this report will again be welcomed by geologists and mineralogists as a source book offering an integrated discussion and summation of world wide progress and results in geological age determination studies.

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THE FORMATION OF MINERAL DEPOSITS, by Alan M. Bateman. John Wiley & Sons, Inc., New York. 371 pp. 1951. $5.50.

The Formation of Mineral Deposits is a partly reconstituted, streamlined version of Part I (Principles and Processes) of Bateman's well known larger textbook, *Economic Mineral Deposits*, " . . . written," as the dust jacket states, "in language as non-technical as possible . . . ." Some of the illustrations are new; others are repeated from the more advanced book. The organizational patterns of the two works are very similar. Chapter subjects in the new book include: materials of mineral deposits, history of their study, their relation to igneous activity, mineralizing solutions, magmatic processes, contact-metasomatism, hydrothermal processes, sedimentary, weathering and ground water processes, metamorphic processes, controls of mineral localization, exploration and mineral resources. Despite its general title the book is concerned mainly with mineral deposits of *economic significance* and is not primarily a textbook on mineral paragenesis. The book has a well-considered scope, and every effort has been made to provide background information for the discussion of the more advanced ideas presented. Despite the author's statement that "A knowledge of mineralogy is not prerequisite," it is difficult to believe that average readers without a command of basic mineralogy and geology can assimilate the work completely. Nevertheless it goes farther than any other available book toward accomplishing its aim, namely "to serve general readers interested in mineral substances, and scientists, engineers, industrialists, and others who deal with the mining profession and business, as well as students who desire collateral reading in other courses or in a brief course in mineral deposits." For these the book can be recommended most strongly.

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EINFÜHRUNG IN DIE KRISTALLOPTIK by EBERHARD BUCHWALD. Sammlung Göschen, Band 619, Walter de Gruyter & Co. 4th edition. 138 pages, 121 text figures. 1952. DM 2.40.

Professor Buchwald's (Jena) simplified introduction to the optical properties of crystals is one of a long series of small (4″×6″) books published as the Göschen collection, a series apparently similar to the College Outline Series published by Barnes and Noble. Following a brief introduction and a short discussion of crystallography, the book is divided into four parts. The first part is titled "Double refraction and polarization," containing in addition discussions of optical surfaces, index of refraction, and conical refraction. "Interference phenomena in polarized light," both parallel and convergent, comprises the second part. The third part contains a discussion of "crystals showing optical rotation and absorption." In an attempt to explain further the observations of the first three parts, the fourth part contains a discussion of the behavior of light in the crystal structure; it is entitled "Lattice optics of the visible spectrum."

Not only is the organization foreign to most texts on optical mineralogy, although nonetheless logical, but the subject content is different and refreshing. The book is concerned solely with the theories and proofs of the theories on the behavior of light in crystals; no consideration is given to optical mineralogy or to the microscope. The discussion is most clear and understandable for such an abbreviated treatment of a complex subject, although some American readers will find the German somewhat difficult.

From past reviews of earlier editions in the *Centralblatt*, this book apparently has been popular with students, for whom it is written. It contains much clarifying and additional material to that found in texts on optical mineralogy. Also from past reviews, it appears that this edition represents little change from the third edition, but considerable change from the first two editions, which contained less discussion of anisotropic crystals and of the electromagnetic wave theory, and more treatment of the effects of physical variables, such as temperature, on the optical constants.

The book is well printed on good paper, and has paper covers. It is most useful for its discussion, albeit too brief, of the electromagnetic wave theory, proofs of laws of optical crystallography, and of the behavior of light in the crystal structure.

GEORGE J. NEUERBURG

GIANTS OF GEOLOGY by CARROLL LANE FENTON AND MILDRED ADAMS FENTON. Doubleday & Company, Inc., Garden City, New York. 1952. Price $3.50.

Geology as an organized body of scientific information is less than 200 years old. However people have been making observations of geological phenomena for more than 2,000 years. The history of Geology is naturally closely associated with the men who have worked in this field and Giants of Geology introduces us briefly to some of these early observers. As early as 585 B.C. Thales of Miletus was studying the Nile delta and the deposition of silt by the famous Meander River. The celebrated philosopher Aristotle (born 384 B.C.) made observations on the stars and the earth. Pliny, who perished in the eruption of Mount Vesuvius in the year 79 A.D., wrote Natural History in which he describes earthquakes, and comments on the occurrences of gold, silver, and iron.

Many workers in the early history of Geology were greatly influenced and often hampered by narrow theological concepts which extend down to recent times and are especially evident in the fields of Evolution and Paleontology. There were fierce conflicts concerning the nature of fossils and some of the explanations that were given to account for these organisms are absurd and grotesque. The great artist, Leonardo da Vinci (1452–1519) gave one of the first correct explanations of the occurrences of fossils in rocks.

Nicolaus Steno, born at Copenhagen in 1638, was greatly puzzled when he found solid shells enclosed in solid rock. He correctly assumed that these shells had once belonged to living animals but larger bones and teeth he thought must have belonged to elephants which Hannibal used in his war against Rome in 218 B.C.

Geological thinking has often been dominated by strong personalities. This may retard the growth of a young science just as fixed ideas always do but fortunately there have always been dissenters in Geology who refuse to accept the dictates even of so-called authorities.

Abraham Gottlob Werner was one of these strong characters. He was born in 1749 and spent much of his life around Leipzig. Werner did not travel extensively and he apparently read very little yet he produced a booklet of 28 pages in which he undertook to tell the complete story of the earth. Werner attracted many enthusiastic students who roamed widely in search of illustrations of the master's ideas. James Hutton was one of the rebels who attacked Werner's system with great success. Hutton believed that the face of the earth has undergone many changes and thus he is in agreement with modern geological thought. Hutton's great work was entitled "Theory of the Earth, With Proofs and Illustrations."

Charles Lyell's famous work, the Principles of Geology, was a sensation and helped greatly to establish geology as a sound and very reasonable science. He traveled widely and observed keenly and was always searching for new material. He visited Canada and the United States in 1841 and gave a famous series of lectures in Boston. The Principles grew with each successive edition. One of these editions contains fifteen chapters on Darwin's Origin of Species. Lyell accepted the main conclusions of Darwin with enthusiasm. He died in 1875, a greatly respected man, and his friends asked that he be buried in Westminster Abbey.

Giants of Geology thus carries the story of geology down through many famous persons into recent times. The foibles of the great are mentioned and we see many of them as fine, friendly characters who believed in the great science of geology and many of these men were inspiring teachers. They have enriched the subject of geology and have helped many people to enjoy the earth upon which we live.

Giants of Geology is written with a light touch but, after all, geologists have their lighter moments. The book should interest the general reader and students of geology will find it a valuable store of information on the history of their subject.,

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METEORITE COLLECTIONS IN HUNGARY. (MAGYARORSZÁG METEORIT-GYÜJTEMÉNYEI) BY TOKODY (LÁZLÓ) AND DUDICH NÉE VENDL (MÁRIA). Budapest (1951).

This book of 102 pages is mainly a list in Hungarian and English of the meteorites in the National Museum of Natural History in Budapest. The list is in duplicate, the falls being arranged first alphabetically by locality of fall; and again according to the classification of Prior. There is no descriptive matter except the weight of each specimen but the total weight of each fall is not indicated.

According to a very brief introduction the first meteorite was acquired in 1815. At present 484 localities are represented by 1295 specimens. There are pieces of all falls (12 stones and 4 irons) that had fallen in Hungary before 1918. There are only 45 falls in the collection dated later than 1900 and the latest fall noted was of 1931.

Three much smaller collections of meteorites in other Hungarian institutions are also listed in the same way.

C. PALACHE,
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NEW MINERAL NAMES

Belyankinite—a new mineral

V. I. Gerasimovsky and M. E. Kazakova

Doklady Akad. Nauk. SSSR, **71,** No. 5, 925–927 (1950); from a translation kindly made by Mr. V. L. Skitsky.

Chemical Properties: Two analyses gave (1. by T. A. Burova, 2. by M. E. Kazakova):

	SiO_2	ZrO_2	TiO_2	$(Nb, Ta)_2O_5$	Al_2O_3	Fe_2O_3	MnO
1.	3.96	6.64	48.76	7.16	0.46	—	none
2.	2.80	6.56	48.19	7.51	0.24	1.85	0.04

	MgO	CaO	Na_2O	K_2O	H_2O^+	H_2O^-	Sum
1.	none	6.72	0.55	trace	8.35	17.21	99.81[a]
2.	0.14	6.40	0.23	0.20	7.20	18.50	99.86[b]

[a] Also reported SrO none, rare earths none.

[b] Also reported CO_2, Cl, F none.

Spectrographic analysis showed the presence of small amounts of Hf and Pb and a trace of Cu, and showed that Nb predominates considerably over Ta.

This gives the empirical formula: $2CaO\cdot 12TiO_2\cdot 0.5Nb_2O_5\cdot ZrO_2\cdot SiO_2\cdot 28H_2O$. [Another form of calculation gives $Ca(Ti, Zr, Si, Nb)_6O_{13}\cdot 14H_2O$. M. F.]

The method of analysis is given in detail. The mineral is decomposed completely by hot HCl.

Infusible before the blowpipe. Thermal analysis gave two endothermic effects, at 150° and 400–450°, and an exothermic reaction at 750°.

Physical and Optical Properties: Occurs in masses up to $20\times 12\times 0.5$ cm. Orthorhombic or monoclinic, from the optical data.

Color light yellow to brownish-yellow. Luster glassy to oily, pearly on the cleavage surface. Cleavage perfect, in one direction, fractures uneven. Hardness = 2–3, G. = 2.32 to 2.40.

Optically biaxial negative, with indices of refraction $n\mathrm{X}=1.740$, $n\mathrm{Y}=1.775$ to 1.780; $n\mathrm{Z}-n\mathrm{Y}=0.002$ to 0.003. Pleochroism distinct; X = brown to dark brown, Y and Z = light brown to yellow brown.

X-ray powder photographs (Cu and Fe radiation) gave no lines, but the Laue diagram indicated some crystallinity.

Occurrence: Belyankinite occurs in nepheline syenite pegmatite composed mainly of microcline, nepheline, and aegirite; the nepheline replaced in part by zeolites. Belyankinite occurs in aegirite and sometimes in microcline; it was formed simultaneously with fluorite, but prior to aegirite. The outer parts of the pegmatite contain eudialyte, ramsayite, and lamphrophyllite. The locality is not given (Kola Peninsula?).

Name: For D. S. Belyankin, Russian mineralogist and petrographer. Not to be confused with the fluoride belyankite, see p. 785.

M. F.